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Title of Thesis: "HAPSITE® Gas Chromatograph/Mass Spectrometer (GC/MS)
Variability Assessment"

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Variability Assessment**

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ABSTRACT

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The HAPSITE® portable gas-chromatograph-mass spectrometer (GC-MS) instrument was analyzed for accuracy and variability. Fifty HAPSITE® instruments were tested against 35 chemicals at 50 and 200 parts per billion concentrations. A standard one-minute sampling method and a tri-bed concentrator (Carbotrap Y/Carbotrap and C/Carboxen 1018) were used. The precision was measured with the percent relative standard deviation, which ranged from 10 to 72% for both concentrations. One source of variation was identified in the HAPSITE® internal air sample pump. The pump flow rate was set at 100 ml/min but actual flows ranged from 49 to 126 ml/min. No clear trends were observed based on the age or the location of the instruments. The HAPSITE® instruments tested showed a -100 to +340% average percent difference from the expected concentration. With improvements to the internal air sample pump and more accurate calibration curves the HAPSITE® portable GC-MS can be a better on-scene quantitative instrument.

HAPSITE® Gas Chromatograph/Mass Spectrometer (GC/MS)
Variability Assessment

by

Michael A. Skinner, Capt, USAF, BSC

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CHAPTER 1 - Introduction

General Background

The need for rapid response chemical detection instruments has received a great deal of attention in the post-September 11 world [Belke, 2004]. It is critical that first-response personnel be able to characterize the chemical hazards associated with a response. A military response, accident or act of terror is already a stressful situation but the situation becomes much more challenging in an uncharacterized chemical environment that involves chemical warfare agents (CWA) or toxic industrial chemicals (TIC). Gas Chromatography/Mass Spectrometry (GC-MS) technology can provide the ability to characterize and identify unknown chemicals during an emergency situation. Identifying unknown chemicals enables authorities to take more precise steps necessary to protect the population and incident responders for the specific hazard. GC-MS provides the ability to quantify the concentration of the chemicals present and thus the specific health risk posed by the chemicals [Nation Institute of Justice, 2000].

In the past, GC-MS systems were operated only in a controlled laboratory setting where wet chemistry procedures could be performed and bulky supplies such as compressed gas cylinders were readily available. The traditional sampling and analysis methods, using lab based GC-MS, function well for, non-emergency situations but are too time consuming when information is needed quickly. With the traditional method, extensive time is required to collect the unknown air sample onto a sorbent media (typically a tube filled with activated charcoal), package and ship the sample to a lab for analysis. There is a need to take the GC-MS technology into the field for rapid chemical identification at a response scene.

Recent developments in portable GC-MS units bring this technology to an incident response and enhance the capability of Department of Defense health assessments. These assessments include the comprehensive health surveillance of all military personnel during active Federal service [DODD 6490.2, 2004]. Additional assessments require the collection and analysis of exposure data in a timely manner [DODI 6490.3, 1997]. While these assessments require instrumentation for monitoring general health threats, the need for emergency response equipment to provide health risk information in a timely manner is also required [AFPD 10-26, 2001].

Inficon HAPSITE®

GC-MS is a powerful technology and considered the "gold standard" for identifying unknown chemicals because it can separate and identify chemicals individually. The GC is typically a coiled 30-meter capillary column with a small diameter that separates a complex mixture of volatile organic compounds (VOC) into individual chemicals. It does this because some chemicals will travel down the GC column faster than others based on the physical properties of the chemicals, such-as: polarity, boiling point, molecular weight. Moving the chemicals through the column requires the use of a carrier gas, typically helium, hydrogen or nitrogen. The MS uses mass spectral data to identify the chemicals as they elute from the GC. The mass spectral data is like a chemical fingerprint matched against a spectral library of chemicals to find the closest match. The retention time of a chemical through the GC column combined with the mass spectral data and peak intensity are used to identify an unknown chemical with a high degree of accuracy. The peak intensity provides a means to determine

the chemical concentration. The GC-MS combination allows a user to identify and quantify volatile or some semi-volatile chemicals in a mixture [McMaster, 1998].

The Inficon® portable GC-MS called HAPSITE® uses the same theoretical principles as any other GC-MS. The HAPSITE® is a unique version of a GC-MS because it is small and lightweight. Its dimensions are 18" x 17" x 7" and it weighs 35 lbs. It is designed to be worn as a backpack, making this GC-MS system the first "man-portable" system. The carrier gas, which is traditionally a large compressed gas cylinder, is compressed nitrogen in a container about the size of a typical 12 oz. aerosol can. Advances in technology have reduced the size of the GC-MS components enabling the HAPSITE® system to be taken directly to an incident involving unknown chemicals for near-real-time analysis. The HAPSITE® draws samples directly from the air, which is different from laboratory GC-MS systems that typically rely on liquid injection. Direct air sampling avoids wet chemistry manipulations that are too difficult and time consuming to perform in a response situation [Inficon®, 2001].

Other unique features of the HAPSITE® include a three-meter pre-column located before the GC column and a membrane located between the GC and the MS as illustrated in Figure 1-1. The pre-column uses nitrogen carrier gas to back flush, which purges low volatility compounds and prepare the column for the next sample without interference. This pre-column keeps the extremely slow moving large compounds with molecular weights above 300 atomic mass units (amu) and boiling points above 280 °C from plugging the column and affecting the analysis of other constituents. It also reduces the possibility of cross-contaminating follow-on samples. This is a limitation of the HAPSITE® instrument compared to other GC-MS instruments that are able to identify compounds with molecular weights above 300 amu. The primary column used in the HAPSITE® is a 100%

dimethylpolysiloxane capillary column (0.32 mm diameter and 30 m long). Just after the GC and before the MS is a semi-permeable membrane made of a 70% dimethyl silicone/30% polycarbonate. The membrane allows volatile, and some semi-volatile, organic compounds to enter the MS, while excluding inorganic constituents, such as the nitrogen carrier gas.

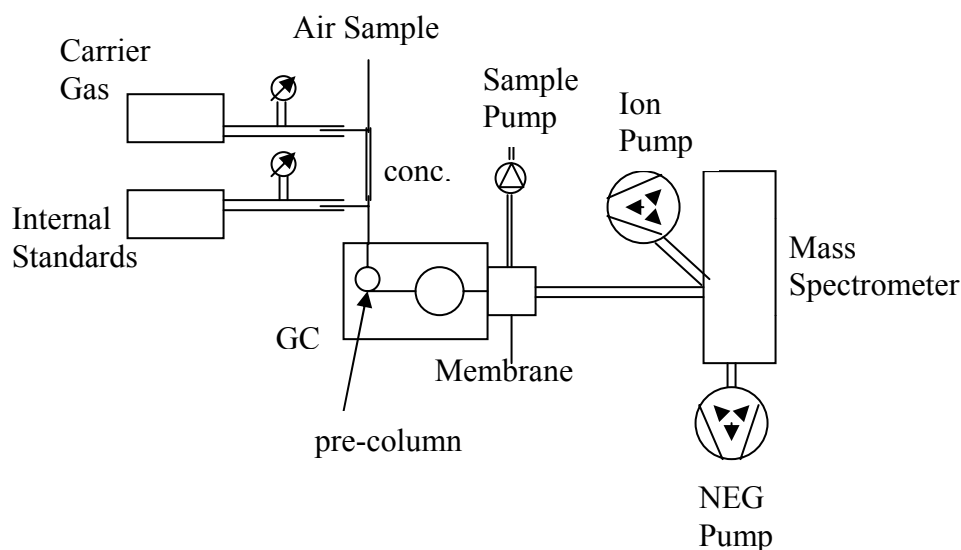


Figure 1-1: Diagram of key components of the HAPSITE® GC-MS. GC includes the concentrator (conc.), three meter pre-column, and 27 meter column.

The HAPSITE® uses an internal standard mixture, contained in a small canister, of 1,3,5 tris-trifluoromethylbenzene (TRIS) and bromopentafluorobenzene (BPFB). The internal standard concentrations are approximately 100 parts per billion by volume (ppbv) for TRIS and 50 ppbv for BPFB. More precise values for each standard are digitally stored on a chip at the bottom of each canister and read by the HAPSITE® during operation. This internal standard mixture is used to optimize or “tune” the MS and to provide a field estimate of chemical concentration by comparing the known volume and peak intensity for the internal standard to the peak intensity of the sampled chemical [Inficon, 2001].

This Study

The HAPSITE® has been purchased by many agencies involved with incident response. The Army National Guard Civil Support Teams (CST), the Marine Chemical Biological Immediate Response Force (CBIRF), Navy Environmental and Preventive Medicine Units (NEPMU), Air Force Bioenvironmental Engineers (BEE), Army Area Medical Laboratories (AAML), and civilian agencies have collectively purchased approximately 200 HAPSITE® instruments. The number of HAPSITE® instruments used by first-responders has increased the need to study ways to optimize its use.

Very limited work has been done to test the variability between HAPSITE® instruments. It is uncertain if a calibration curve developed on one, or a few, instrument(s) can be used by other instruments for reliable quantification. Results of this study give the operators in the field an understanding of the response variability between HAPSITE® instruments against known chemical concentrations. Knowing instrument variability allows greater confidence in the chemical concentration estimates and more trustworthy risk assessments, enabling responders to make informed decisions during an incident. The goal of this research is to provide information on the variability that exists between HAPSITE® instruments. Calibration curves are necessary to quantify the concentration of a chemical analyzed by GC-MS. The traditional licensed laboratory must create a five-point calibration curve for each chemical on each instrument. This must then be checked daily with a "calibration verification" standard for each chemical to ensure proper calibration. A new calibration curve is needed when the "calibration verification" shows a 20% drift [EPA Method 8260b, 1996].

This study uses a single calibration curve for 50 instruments. The internal standards for the HAPSITE® provide a reference to compare the response of an instrument to another chemical. The concern with using one calibration curve for multiple instruments is a loss of accuracy. Each instrument will vary in its response to individual chemicals and this study tests how well the internal standard comparison compensates for the variability between instruments.

Research Question: How much variability exists between HAPSITE® instruments and what are the major sources of variability between instruments?

Specific Aims:

1. Test 50 fielded HAPSITE® instruments against 35 chemicals at two known chemical concentrations (approximately 50 and 200 parts per billion).
2. Develop 95 percent tolerance intervals for each chemical.
3. Identify trends in instrument response by chemical compound, instrument age, geographic location, or other factors; and determine possible causes for these trends.

CHAPTER 2- Literature Review

Few studies have been performed using the HAPSITE® portable GC-MS because its widespread use in emergency and military applications began just after the terrorist attacks on September 11, 2001. However, there are some studies with the HAPSITE® involving hazardous material sites, groundwater contamination and chemical warfare agents. Generally these studies were done to determine chemical detection limits and operating conditions that may effect the performance of the HAPSITE® system.

In 2001, the Environmental Protection Agency (EPA) conducted a study to determine the precision and accuracy of the HAPSITE® for groundwater contamination. The study was performed at the Department of Energy Savannah River site, near Aiken, South Carolina and McClellan Air Force Base, California [EPA, 2001]. The evaluators used the HAPSITE® headspace-sampling unit to identify chemicals from a water matrix. The headspace-sampler bubbles nitrogen gas through the water sample to drive volatile chemicals from the water to the HAPSITE®. The pocket of air above the liquid is referred to as the headspace. A split sample was used in this EPA study to determine the HAPSITE® performance. The results of the headspace samples from the HAPSITE® were compared to sample results sent to a certified laboratory using an Agilent 6890 GC and 5973 MS. The following six chlorinated VOC compounds were evaluated in this study at nine different concentrations ranging from 5 µg/L to 890 µg/L:

- Trichloroethene,
- Tetrachloroethene,
- 1,2-Dichloroethane,
- 1,1,2-Trichloroethane,
- 1,2-Dichloropropane,
- *trans*-1,3-Dichloropropene

To determine analytical precision of the HAPSITE®, four replicate samples were run for six analytes on the HAPSITE® instrument. A reference laboratory also tested the six analytes for comparison. The HAPSITE® percent relative standard deviation (%RSD) ranges are shown below for each chemical. The HAPSITE® %RSD range for all six analytes was 2 to 28%. The median %RSD for the HAPSITE was 12%. This compares to the reference laboratory, which had a median value of 7%. The ranges of %RSD values for the six analytes are as follow:

- Trichloroethene 7 to 18%
- Tetrachloroethene, 6 to 22%
- 1,2-Dichloroethane, 2 to 12%
- 1,1,2-Trichloroethane, 8 to 28%
- 1,2-Dichloropropane, 7 to 21%
- trans-1,3-Dichloropropene, 7 to 17%

The analytical accuracy of the HAPSITE® was measured by comparing the HAPSITE® results to a known concentration in spiked samples. The absolute percent difference (APD) is used to measure accuracy. The APD is the difference between the known concentration of chlorinated VOC in the water sample and the concentration as estimated by the HAPSITE®. The APD for all reported compounds from both sites had a median value of 8%. This compares well with the APD from the reference laboratory, which had a median value of 7%. There was good correlation between the reference laboratory and the HAPSITE® measurements. The correlation coefficients (r) for all compounds detected by both the HAPSITE and laboratory was 0.983 at Savannah River and 0.978 at McClellan for concentrations less than 100 µg/L. The r-values above 100 µg/L were 0.996 for Savannah River and 1.000 for McClellan. The authors note that these "correlation coefficients reveal a highly linear comparability relationship between HAPSITE and laboratory data" [EPA, 2001].

Studies on the effectiveness of detecting chemical warfare agents (CWA), with the HAPSITE®, have been accomplished by the Army Research Lab at Edgewood. One study determined the instrument identification level (IIL) for the CWA sarin (GB), soman (GD), and mustard (HD) and whether diesel fuel caused an interference problem. The IIL is the minimum chemical concentration that the HAPSITE® can accurately identify the compound, this means that the instrument provided a similarity index (SI) >700 for this study. The SI is used to show how well the mass spectrum of the HAPSITE® instrument compares to the National Institute of Standards and Technology (NIST) library spectrum, with a perfect match being 1000. Each chemical has a unique IIL based on the ability of the GC to separate chemicals and the ability of the MS to detect the mass fragments generated. Seven instruments were used for this test and the parameters included: 60-second sampling time, 60°C initial column temperature, followed by a 30°C/min temperature ramp to achieve a 200°C final column temperature [Edgewood 2003]. The ILL for GB, GD, and HD, without interference, are shown in Table 2-1.

The Edgewood study also provided information on identification of CWA in the presence of diesel fuel. The set-up for this portion of the test involved mixing the CWA with solutions of diesel fuel in hexane ranging from 0.0001% to 0.4% to determine an acceptable level of interference. The study found that a 0.3% diesel fuel in hexane dilution was high enough to interfere with visual identification of the CWA at the IIL. 10µl of the 0.3% diesel fuel solution and 10µl of CWA at a given concentration were mixed and then introduced into the instruments via the sample probe. The CWA IIL in the presence of diesel fuel was determined by the concentration of CWA necessary to be identified with an SI>700. Table 2-1 shows the ILL for GB, GD and HD with 0.3% diesel in hexane interference.

Table 2-1: IIL for GB, GD and HD and interference with diesel fuel.

	Sarin (GB)	Soman (GD)	Mustard (HD)
IIL (no interference)	0.08 mg/m ³	0.13 mg/m ³	0.07 mg/m ³
IIL (0.3% diesel added)	0.15 mg/m ³	0.48 mg/m ³	0.34 mg/m ³

In the Edgewood (2003) study, blank samples were taken after each experimental sample to test for carryover, chemicals left in the column or concentrator after a sample that are observed in the next sample. Carryover was tested by running a blank sample after the chemical agent sample to test for the presence of the chemical agents still seen in the chromatogram of the blank. Carryover was defined as a SI of >400 for any of the CWA. Agent carryover in a blank sample was found in one of the seven instruments tested at the IIL for GB and GD. No carryover was detected at the IIL for HD.

A source of interference during this study came from the HAPSITE® internal standard, BPFB, which had the same retention time as GD, causing co-elution. The temperature ramping in the GC was increased from 20 °C/min to 30 °C/min and the internal standard automatic injection was turned off to eliminate the co-elution problem [Edgewood 2003].

Another study was used to determine the effects of extreme temperature (-32 to 43 °C, -25 to 110 °F) and relative humidity (0 to 100%) on the IIL for GB, GD, and HD. While the freezing point of HD is 14.5 °C, vapors were detected at 1.7 °C. However, no test for HD vapor was performed at -32 °C. The sampling method for the two HAPSITE® instruments was exactly the same as the earlier Edgewood study for determining IIL. Varying the temperature and the relative humidity would not be expected to have a large impact since the GC-MS system is designed to separate and identify chemicals based on chemical characteristics. The GC-MS process uses heat to keep the analytes in a vapor phase while in the instrument. The sampling probe for the HAPSITE® is maintained at 40 °C (104 °F) to

keep any volatile chemical in the vapor phase until it reaches the sample loop trap, which is at 60 °C. This study showed negligible impact on operations of the HAPSITE® due to changes in the temperature and relative humidity. The changes observed were due to the chemical characteristics of the CWA. The lower the temperature the more CWA had to be used to produce a vapor concentration high enough to be identified. Table 2-2 shows the average of the triplicate samples run for each agent at each physical condition in mg/m³ [U.S. Army, 2003].

Table 2-2: IIL for CWA at different Temperature and Humidity Levels. (Note: all chemical concentrations in mg/m³.)

Temperature (°C)	%RH	Sarin (GB)	Soman (GD)	Mustard (HD)
43	25	0.04	0.04	0.02
25	25	0.08	0.04	0.04
25	<90	0.01	0.02	0.02
1.7	0	0.01	1.2	0.15
-32	0	4.4	2.1	N/A

Other tests were performed to compare the performance of the HAPSITE® with a field portable Viking® GC-MS, coupled with a solid-phase micro-extraction sampler (SPME), against the CWA: GB, GD, cyclo-sarin (GF) and HD [Smith, 2004]. To draw the air sample from the Tedlar bag, researches attached the HAPSITE® directly to the bag. A one-minute sample time was used to pull the sample into the Tenax concentrator bed. The Tenax concentrator bed is an add-on component for the HAPSITE® developed to reduce the IIL for most CWA. The temperature ramping profile for the HAPSITE® GC started at 70 °C and ramped to 180 °C at 30 °C/min [Smith, 2004].

The HAPSITE® and the Viking® were compared with regard to their ability to sample and to detect components present in a mixture of four volatile CWA. These tests showed that

the HAPSITE® and the Viking® with SPME units successfully identified the G-series nerve agents and HD, with the HAPSITE® needing spectral manipulation for GF and HD to obtain a library match. This study raised some questions on the effectiveness of the HAPSITE® to produce good chromatograms when using a Tenax concentrator. Some of the widths at the base of the peak were measured near 20 seconds, compared to the Viking system peaks at around 1 second. Such broad peaks are undesirable as they may mask another compound with a similar retention time [Smith, 2004].

The Midwest Research Institute (MRI) in Kansas City, Missouri conducted a study to optimize the use of a tri-bed concentrator with TIC. The tri-bed concentrator is made up of three carbon-based sorbent materials. Each is designed to trap chemicals that are polar, semi-polar or non-polar. The three sorbent materials, Carbotrap Y/Carbotrap and C/Carboxen 1018, are used in series and in equal mass proportions. Using a tri-bed concentrator enhances detection of a wider array of chemicals at lower concentrations.

MRI used the tri-bed concentrator in creating five-point calibration curves. They sampled at each concentration in triplicate, for 104 chemicals, 23 chemicals of which were identified in International Task Force (ITF)-40 report [USACHPPM, 2003]. The remaining 81 TIC were added based on a Navy threat assessment of chemicals that could be used in a terrorist attack or potentially hazardous industrial release [Midwest Research Institute, Table 2-7, 2005]. The development of calibration curves for each chemical were completed using four HAPSITE® instruments. The calibration curves from each instrument were averaged to create one curve for each of the 104 chemicals. An example of the calibration curves from the four instruments is shown in Figure 2-1 [Midwest Research Institute, 2005].

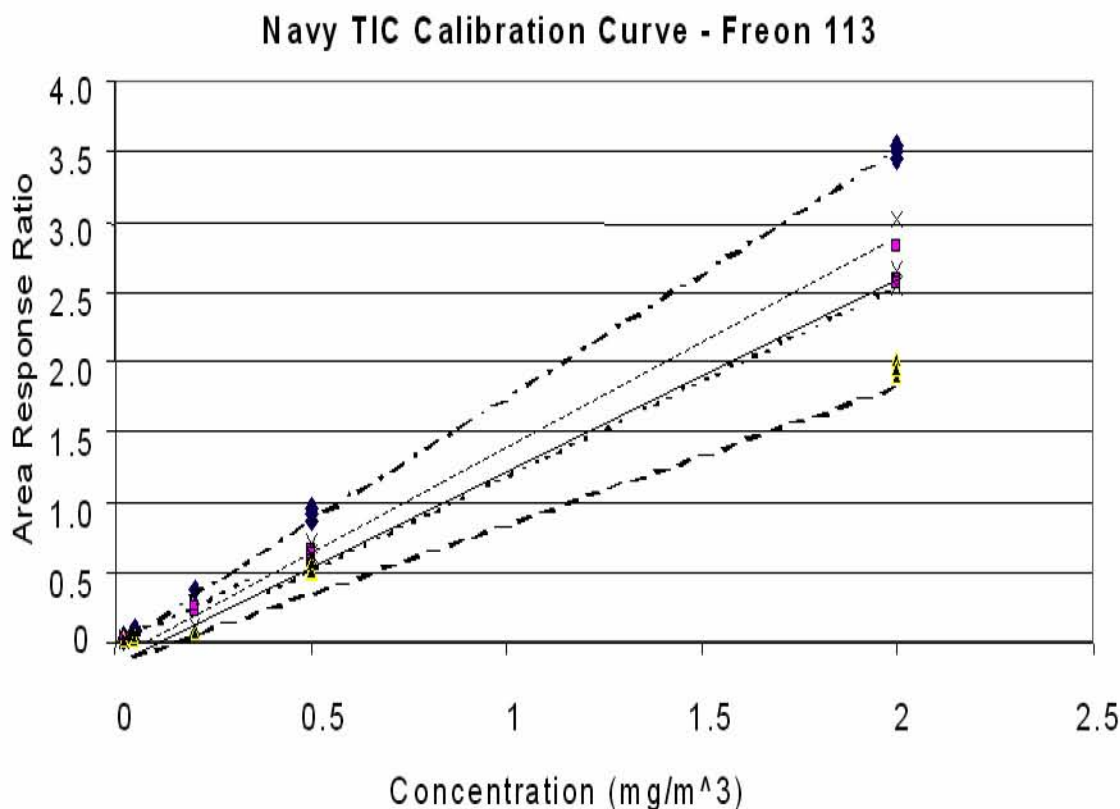


Figure 2-1: Calibration curves from the four HAPSITE® instruments for Freon 113. The solid line represents the average, while dashed lines are the instrument curves. (Note: The area response ratio is a measure of the area under a chromatogram peak and is proportional to increasing concentration.)

The quality of the calibration curves was measured with the %RSD. The %RSD compares the standard deviation to the average at each concentration. This method measures the variability within each instrument for the triplicate runs and it measures the variability between the four instruments. The %RSD ranged from 20%-89% for each chemical between the four instruments in this study. When analyzing the average of the four calibration curves, ten of the 104 analytes had %RSD greater than 50% between instruments. The author concluded that the variability was consistently better within an individual HAPSITE® than the variability between all four instruments, but no %RSD for variability within an instrument was given to support this conclusion [Midwest Research Institute, 2005].

The previous research has been on the capability of the HAPSITE® to detect different chemicals and determine what are the IIL for those chemicals. This paper addresses the ability of the HAPSITE® to estimate the concentration of an identified chemical and how much variability exists in that estimation. Furthermore, this study addresses potential factors that increase the variability.

CHAPTER 3- Methodology

This study will determine the variability that exists between HAPSITE® instruments and the major sources of the variability between instruments. The assessment of variance was accomplished using 50 HAPSITE® GC-MS instruments at three locations, Ft. Leonard Wood, MO (24 instruments), Brooks AFB, TX (12 instruments), and Inficon Maintenance Facility in Syracuse, NY (14 instruments). The HAPSITE® instruments were tested with a standard gas mixture of 35 chemicals at two concentrations, approximately 50 and 200 parts per billion (ppb) (PortaGas, Houston, TX). These chemicals span the spectrum of retention times for the default HAPSITE® method using the tri-bed concentrator, 2 minutes to 15 minutes. The chemicals and their GC retention times are shown in Table 3-1 [Midwest Research Institute, 2005].

Table 3-1: Chemicals Selected for this Study with Retention Times.

Chemical	Retention Time	Chemical	Retention Time
1,2-Dichlorotetrafluoroethane	1:26	1,2-Dichloropropane	3:21
Chloromethane	1:28	Trichloroethene	3:22
1,3-Butadiene	1:28	Toluene	4:51
Vinyl chloride	1:29	Tetrachloroethene	6:22
Chloroethane	1:29	Chlorobenzene	7:32
Freon 11	1:41	Ethylbenzene	8:23
3-Chloro-1-Propene	1:47	m&p-Xylene	8:23
cis-1,2-Dichloroethene	1:48	Styrene	8:50
1,1-Dichloroethene	1:48	o-Xylene	8:56
Methyl bromide	1:49	1,3,5-Trimethylbenzene	10:26
Methylene chloride	1:50	p-Ethyltoluene	10:27
Freon 113	1:51	1,2,4-Trimethylbenzene	10:51
1,1-Dichloroethane	2:02	1,3-Dichlorobenzene	11:03
Chloroform	2:20	1,4-Dichlorobenzene	11:03
1,2-Dichloroethane	2:35	1,2-Dichlorobenzene	11:22
1,1,1-Trichloroethane	2:41	1,2,4-Trichlorobenzene	13:19
Benzene	2:51	Hexachlorobutadiene	13:56
Carbon tetrachloride	2:55		

The 35 chemicals also provide a mix of polar, non-polar and semi-polar compounds to characterize the HAPSITE® across a broad range of chemical polarity. According to the PortaGas Certificate of Accuracy, the compressed gas cylinders are stable at the specified concentrations, $\pm 10\%$, for 6 months. All data collection was accomplished within 6 months.

A two-stage pressure reducer (PortaGas, Houston, TX) was used with each 104 L compressed gas cylinder containing the gas mixture (at 50ppb and 200 ppb). The pressure was reduced, and the gas was vented to the room environment, allowing the instrument to sample near normal atmospheric pressure even though the cylinder pressure was much higher. The vent was fitted with a flow indicator to control the amount of gas being vented. The sampling head of the HAPSITE® was directly attached to the outlet of the pressure reducer through a Teflon® tube, minimizing the possibility of dilution or contamination from the outside air. Having the sample introduced in this manner closely mimics the environmental conditions encountered in the field, while maintaining the control necessary for research.

The calibration curves that were averaged together from the MRI study will be used to evaluate the variability of response for the 50 HAPSITE® instruments tested in this research. The use of an internal standard that is injected at a known concentration with each sample run reduces variability between instruments for quantifying results on many different machines using one calibration curve. The internal standard controls for the differences in MS responses by comparing the peak area from a sample to the peak area of the internal standard, which corrects for minor variations.

GC-MS Set-up

The HAPSITE® method parameters control the length of sampling time, the rate at which the sample moves through the column, the temperature ramping of the column, and the thermal flash of the concentrator. The tri-bed concentrator is used to trap the sample and provide lower detection capabilities. The tri-bed method, using one-minute sample time, has been standardized to identify the compounds listed in the USACHPPM (2003) document as primary threats. The temperature profile in the GC, just after the standardized one-minute sample time, begins with a seven-minute hold at 60 °C followed by a 20 °C/min ramp to 150 °C and then a 10 °C/min ramp to 180 °C, which is then held for 30 seconds. This oven ramping profile provides an analysis time of 15 minutes, shown in Figure 3-1.

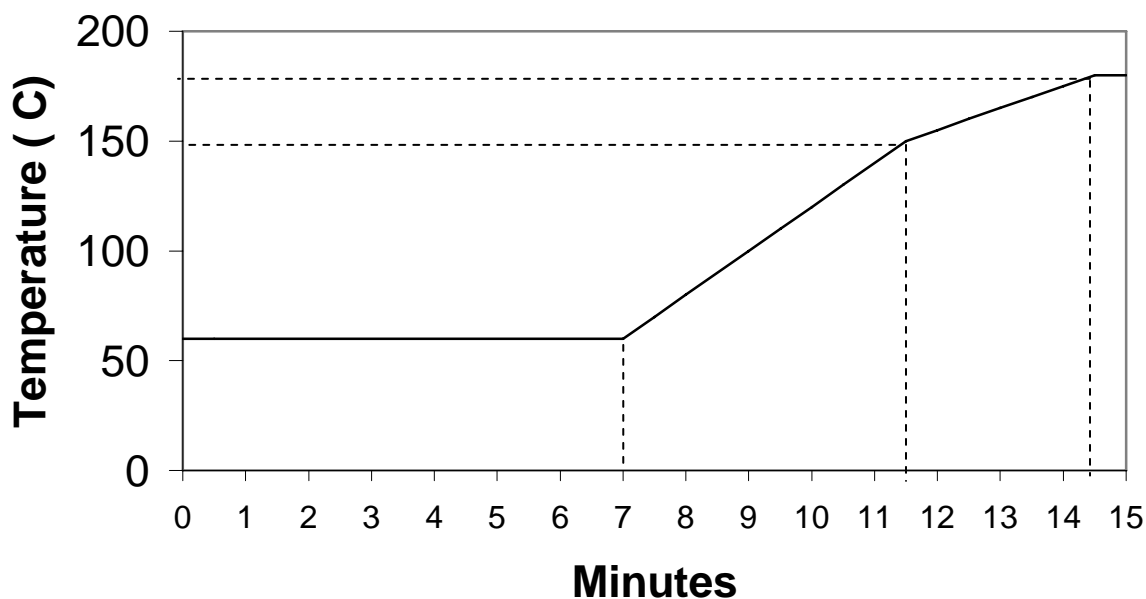


Figure 3-1: GC temperature ramping profile for test method.

Test Protocol

Each HAPSITE® instrument was calibrated to the manufacturer's temperature parameters and the MS was tuned. A basic tune taught to field operators uses three tuning parameters. An advanced tuning method was used for this work to ensure that all of the instruments are functioning to manufacturer specifications. The advanced tuning process included maximizing the response of the MS at the mass ion fragment of 117 atomic mass units (amu) using seven different tune parameters. The 117 mass fragment is especially important for tuning because it is the largest ion peak for the BPFB internal standard. All other mass fragments, including the TRIS mass fragments, are a known percentage of the 117 mass fragment. The remainder of the tuning process optimized the peak resolution and peak quality for all of the mass fragments in the internal standards. The BPFB and TRIS internal standards provide a range of mass fragment peak resolutions from 55 amu to 281 amu that are used to tune the full HAPSITE® detection range of 41 amu to 300 amu.

After tuning, a blank sample was run to test the tri-bed concentrator and internal components for contamination and to check the retention time of the two internal standards. TRIS is expected to elute at approximately 2 minutes and 30 seconds and BPFB at approximately 8 minutes. If the internal standard does not elute at the appropriate time, the column pressure is adjusted so the standard elutes within five seconds of the target retention time. These retention times are the standard times used in creating the quantification report. If the retention time for each internal standard is 10 seconds too high or too low, the internal quantification report will not provide any results. The HAPSITE® instruments in this study were adjusted by the manufacturer to meet the internal standard retention time requirement of

2.5 minutes for TRIS and 8 minutes for BPFB, because this is not normally done by field operators.

The final optimization step included the injection of one μL of a liquid performance standard into the inlet of the HAPSITE® at the beginning of a sampling loopfill. The performance standard, manufactured by Burdick and Jackson Co., (Muskegon, MI), contains the chemicals listed in Table 3-2 in a methanol solution. A small liquid injection is the most accurate way to evaluate the response of the HAPSITE® to a known sample. The HAPSITE® inlet, which is heated to 40°C, vaporizes the liquid and allows the instrument to sample the injected liquid as a vapor.

Table 3-2: Performance standard chemical compounds and concentrations.

Chemical	Target Concentration (mg/L)	Actual Concentration (mg/L)
Fluorobenzene	20	20.5
Chlorobenzene-d5	20	20
Toluene-d8	20	20.4
Dichlorobenzene-d4	20	20
Diethyl Malonate	20	20

The performance standard test uses the 5 minute loopfill with the same GC temperature profile as the 1 minute loopfill (Figure 3-1). The performance standard test is the most accurate way to check the operating conditions of the HAPSITE®; however it is not normally performed during field operations. The results of the performance standard tests were used to only eliminate an instrument from this study. An instrument was eliminated if the response to the performance standard changed by >50% between the beginning and end performance standard tests. No instruments were eliminated from this study.

All of the tests involving the compressed gas cylinders were accomplished by attaching the stainless steel, two-stage pressure reducer to the inlet of the HAPSITE® with a Teflon® tube. The main outlet valve on the compressed gas cylinder was opened fully prior to opening the vented pressure reduction valve and taking the sample. The vented pressure reduction valve was open at the beginning of line purge. Line purge is a one-minute back flush of the HAPSITE® with nitrogen to clear any ambient gases that may be in the system. An air sample is not drawn into the HAPSITE® during the Line Purge. A diagram of the test configuration used in this test is shown in Figure 3-2.

A blank run to clean the concentrator and the column was run between samples for the first four instruments. This was accomplished to assure subsequent tests were not influenced with chemicals that were carried over from the previous test. Since, no peaks were found during the sample blank runs on the first four instruments, there were no sample blanks used between the remaining test runs; however, blanks were run prior to the beginning of the test for each instrument.

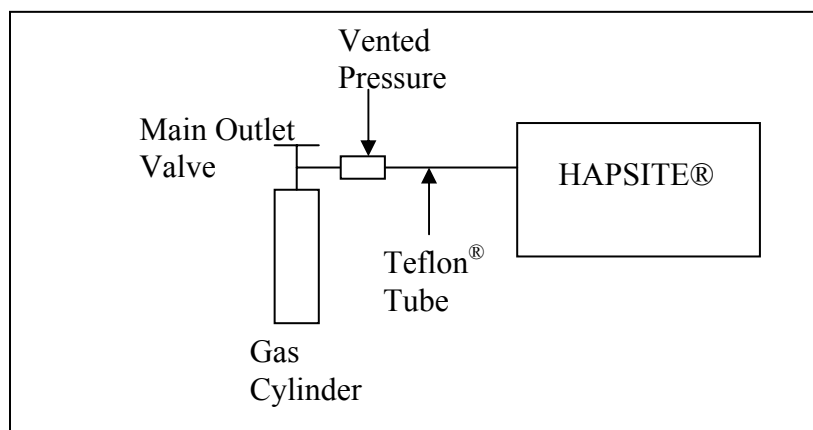


Figure 3-2: Test configuration for sampling compressed gas cylinders with the HAPSITE®

Analysis of Data

The HAPSITE® internal software produced a spreadsheet using the averaged calibration curves created by MRI [Midwest Research Institute, 2005]. In this research, the HAPSITE® software used these curves to compute a concentration estimation for each chemical. The triplicate sample runs on each instrument at the 50 and 200 ppb concentrations were averaged and compared to the cylinder concentrations provided by PortaGas. The triplicate samples provided the within instrument variance. The means from all 50 instruments were used to compute the variance between instruments.

In order to show the variability between instruments, a %RSD across the 50 HAPSITE® instruments was used for each of the 35 chemicals at both concentrations. The %RSD, equation (1), is a comparison of the standard deviation to the mean, where X represents the mean and SD represents the standard deviation for a given chemical across 50 HAPSITE® instruments.

$$\%RSD = (SD/X)*100 \quad (1)$$

Further analysis was needed to determine the usefulness of using one calibration curve for all HAPSITE® instruments. Tolerance limits were chosen to provide this information. Tolerance limits estimate the value range for 95% of all instruments using the same methods as this study. A tolerance interval was chosen because, "Unlike the confidence interval, which estimates the range in which a population parameter falls, the tolerance interval estimates the range which should contain a certain percentage of each individual measurement in the population" [Walpole, 1993]. A tolerance interval allows the results from these 50 HAPSITE® instruments to be applied to all other HAPSITE® instruments. The tolerance limit constant (K) value is 2.065 for N=50 [Walpole, 1993] and equation (2), where

X represents the mean and SD represents the standard deviation for a given chemical for the 50 HAPSITE® instruments tested [Walpole, 1993].

$$\text{Tolerance limit} = X \pm K * SD \quad (2)$$

Additional statistical methods were used to compare the effects that location, age and the HAPSITE® air sample pump flow rate had on the instrument response. Comparing the results for each chemical on all instruments at one of the three locations and comparing them to the other two locations was accomplished using a Tukey's Multiple Comparison test. This tests the significance of the difference for all of the chemicals at their given location.

A Spearman Rank Correlation was used to determine if there was any correlation between the age of instrument and the average response across all chemicals. A rank correlation was used because the age of the instrument was defined by the serial number, not the actual production date. Serial numbers are assigned sequentially from the manufacturer so, production dates can be approximated with the serial number. The serial numbers of the instruments were ranked from the lowest serial number to the highest. The instruments were then ranked by flow rate from lowest to highest. The instrument ranks by serial numbers were also compared to instrument ranks by flow rate.

Finally, a cluster analysis was accomplished to find trends between chemical compounds and their response across all of the instruments. PortaGas provided the expected concentration for each chemical in the gas cylinders and those concentrations varied from 42.7 ppb to 54.5 ppb, and 169.1 ppb to 218.2 ppb in the 50 ppb and 200 cylinders respectively. See Appendix A for specific manufacture concentrations. In order to evaluate the data for similarities in response, the HAPSITE® concentration estimation was normalized to 50 and 200 ppb. Equation (3) was used to normalize the data where NV is the

normalized value, X_c is the average for the specific chemical as quantified by the HAPSITE®, and C_b is the expected concentration from the compressed gas cylinder according to the manufacturer.

$$NV = X_c(50/C_b) \quad \text{or,} \quad NV = X_c(200/C_b) \quad (3)$$

A cluster analysis of the normalized data was accomplished. The analysis identifies the chemicals that responded similarly across the 50 instruments tested [SPSS® 7.5, 1997]. The response of one chemical had to be 95% similar to another chemical to be grouped into a cluster.

Chapter 4 - Results of Analysis

The purpose of this study was to determine how much variability exists between HAPSITE® instruments and the major sources of variability between instruments using the one-minute loopfill method and tri-bed concentrator. Figure 4-1 shows the average of the three replicates for each instrument tested at 50 ppb. Figure 4-2 shows the average of the three replicates for each instrument tested at 200 ppb. The solid line is the cylinder concentration of each chemical as provided by PortaGas. The statistical analysis that follows was based on the data illustrated in figures 4-1 and 4-2.

Another trend observed in Figures 4-1 and 4-2 are that some chemicals responded consistently higher than expected, while other chemicals responded consistently lower. For example, Freon 113 underestimated the expected concentration; 17 ppb when 42 ppb was expected and 70 ppb when 169 ppb was expected. 1,1 Dichloroethene overestimated the expected concentration, estimated at 183 ppb for an expected 43 ppb and 687 ppb for an expected 171 ppb.

To measure the variability between the HAPSITE®, the %RSD for each chemical is plotted in Figure 4-3. Note that there is no clear trend in the %RSD despite whether the HAPSITE® overestimated or underestimated the expected concentration. The only trend that can be seen is that the %RSD are slightly lower for the 50 ppb concentrations where the vast majority range from 10-30% RSD as compared to the 200 ppb concentrations where the vast majority range from 25-60% RSD.

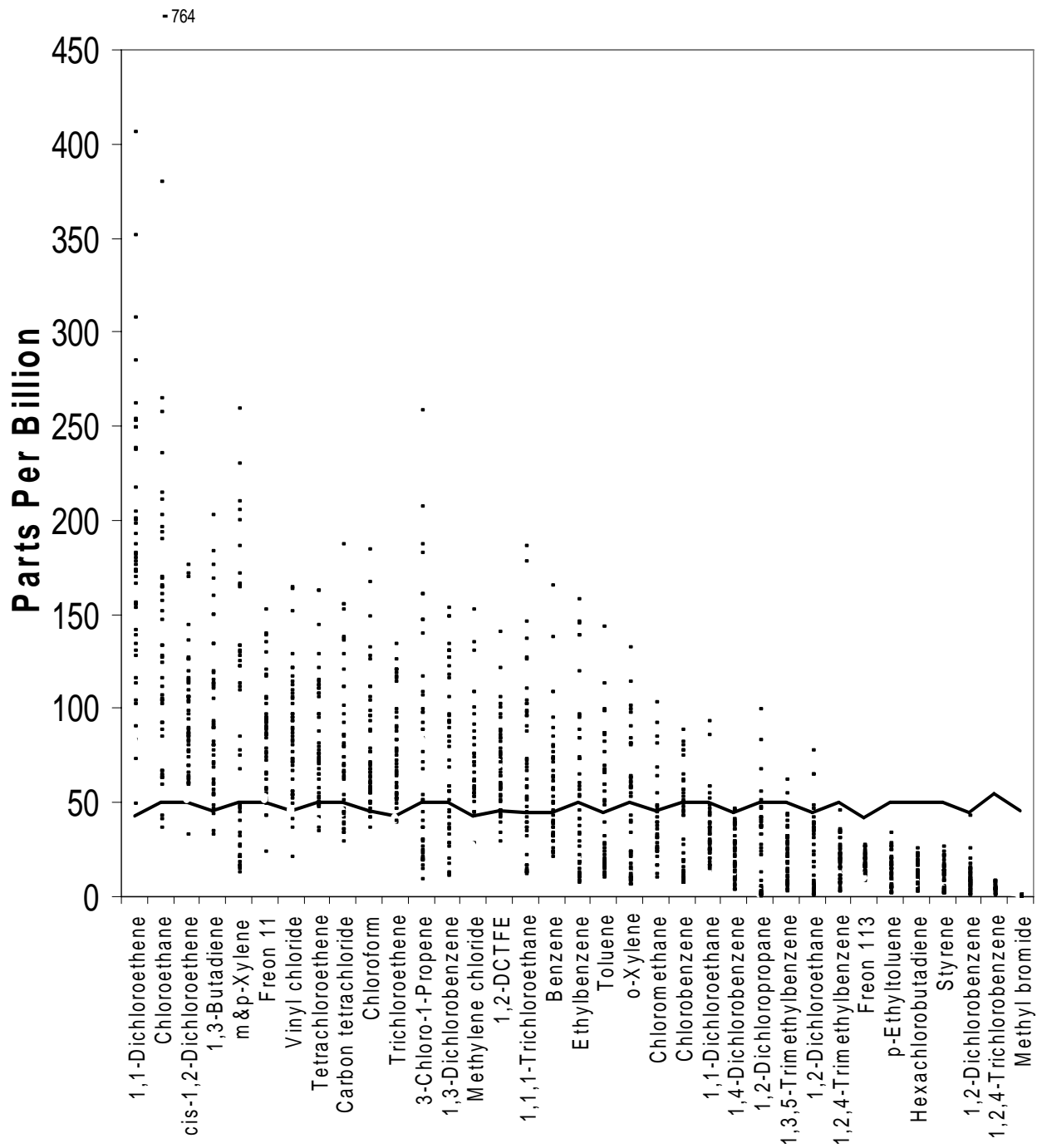


Figure 4-1: Estimated concentration from 50 HAPSITE® instruments by chemical for the 50 ppb concentration. Line indicates the concentration expected from the standard cylinders.

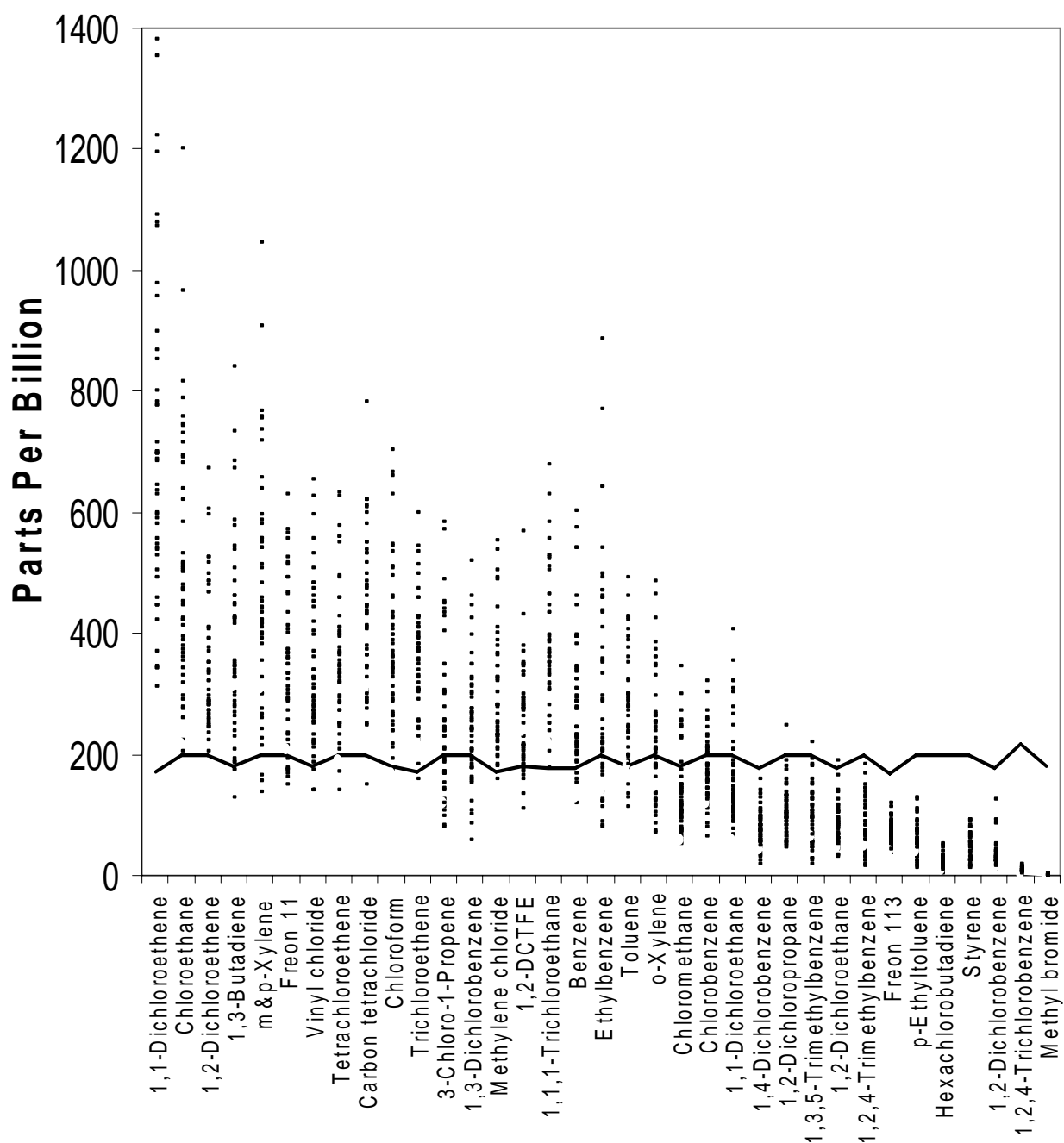


Figure 4-2: Estimated concentration from 50 HAPSITE® instruments by chemical for the 200 ppb concentration. Line indicates the concentration expected from the standard cylinders

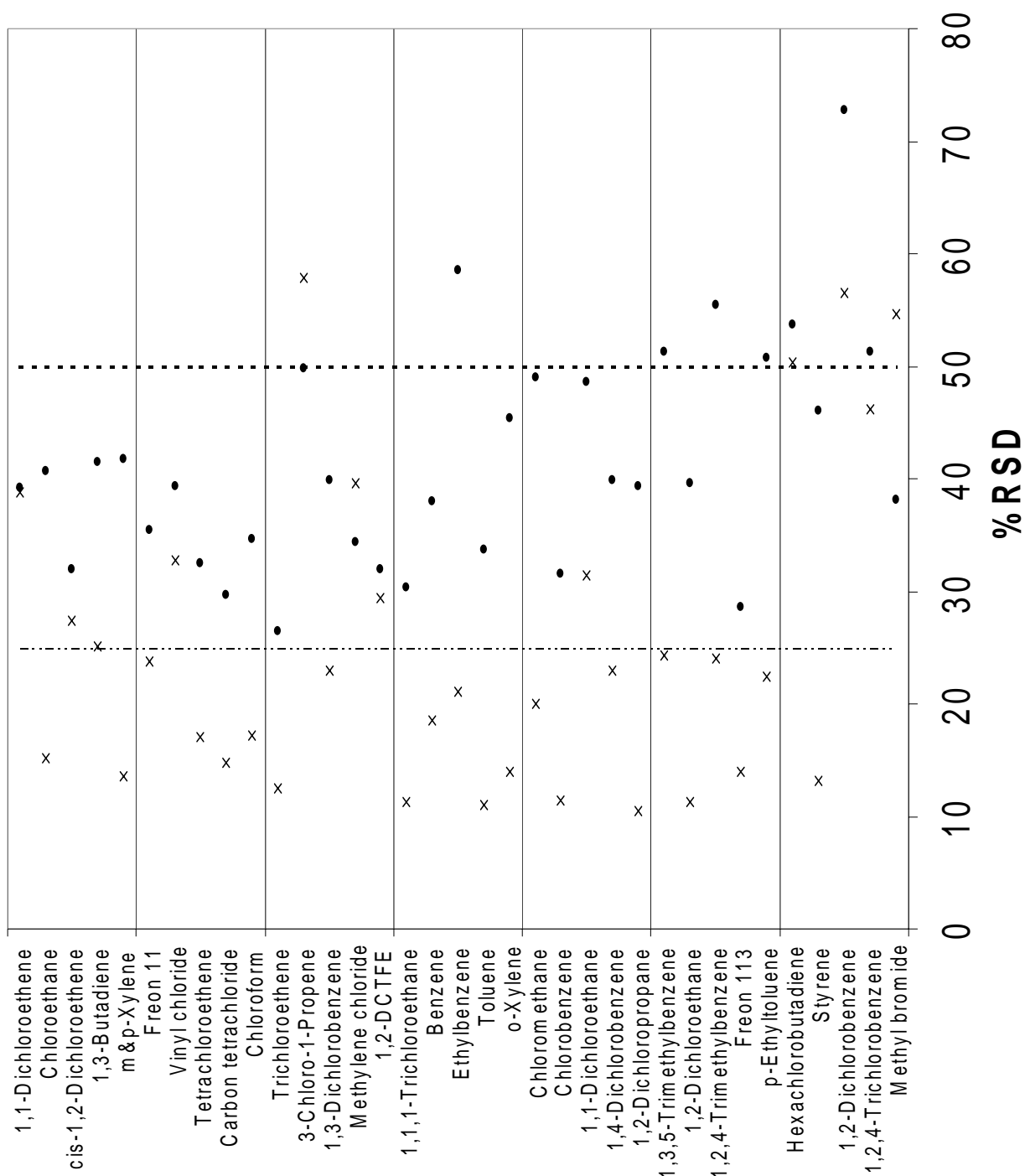


Figure 4-3: %RSD for 50 HAPSITE® instruments for 50(x) and 200 (●) parts per billion tests by chemical.

To test the accuracy of the 50 instruments, the estimate was compared to the expected value from the test cylinders. The APD was calculated for each chemical for the 50 and 200 ppb tests. Figure 4-4 shows the results of this analysis. PortaGas reported a 10% error on the estimated concentration in the test gas cylinders but the APD ranged from -98% underestimated to 350% overestimated. Additionally, the 50 ppb and 200 ppb concentrations show a very close agreement. This implies that the HAPSITE®s were consistent as to whether it would over or underestimate a chemical. This may demonstrate a problem with the accuracy of the calibration curves installed in HAPSITE® software. The data is reasonably precise as noted by the %RSD; however, significantly over or under predicts the actual concentration as noted by the APD. It is possible that a reevaluation of the calibration curves installed into the HAPSITE® software could significantly improve the estimated concentrations provided by the HAPSITE®.

Tolerance Limit Analysis

Figures 4-5 and 4-6 show the tolerance limits calculated from this study by chemical at 50 ppb and 200 ppb respectively. The tolerance limits provide the range that 95% of all instruments are predicted to be within. On the following graphs the "whiskers" show the tolerance limits and the "box" shows one standard deviation above and below the mean [See Appendix B for table of data]. Note that the tolerance limits for the 12 chemicals on the right side of Figure 4-5 and Figure 4-6 do not include the expected concentration denoted by the horizontal line. This means that 95% of all instruments would underestimate these 12 chemicals. Also, the tolerance intervals for the 11 chemicals to the left of both figures significantly overestimate the expected concentrations. So this figure illustrates that the majority of chemicals are significantly over or underestimated by HAPSITE®. For the 50 ppb concentrations, only 6 of 34 chemicals are within one standard deviation of the expected

concentration and 8 of 34 chemicals are within one standard deviation for the 200 ppb concentrations.

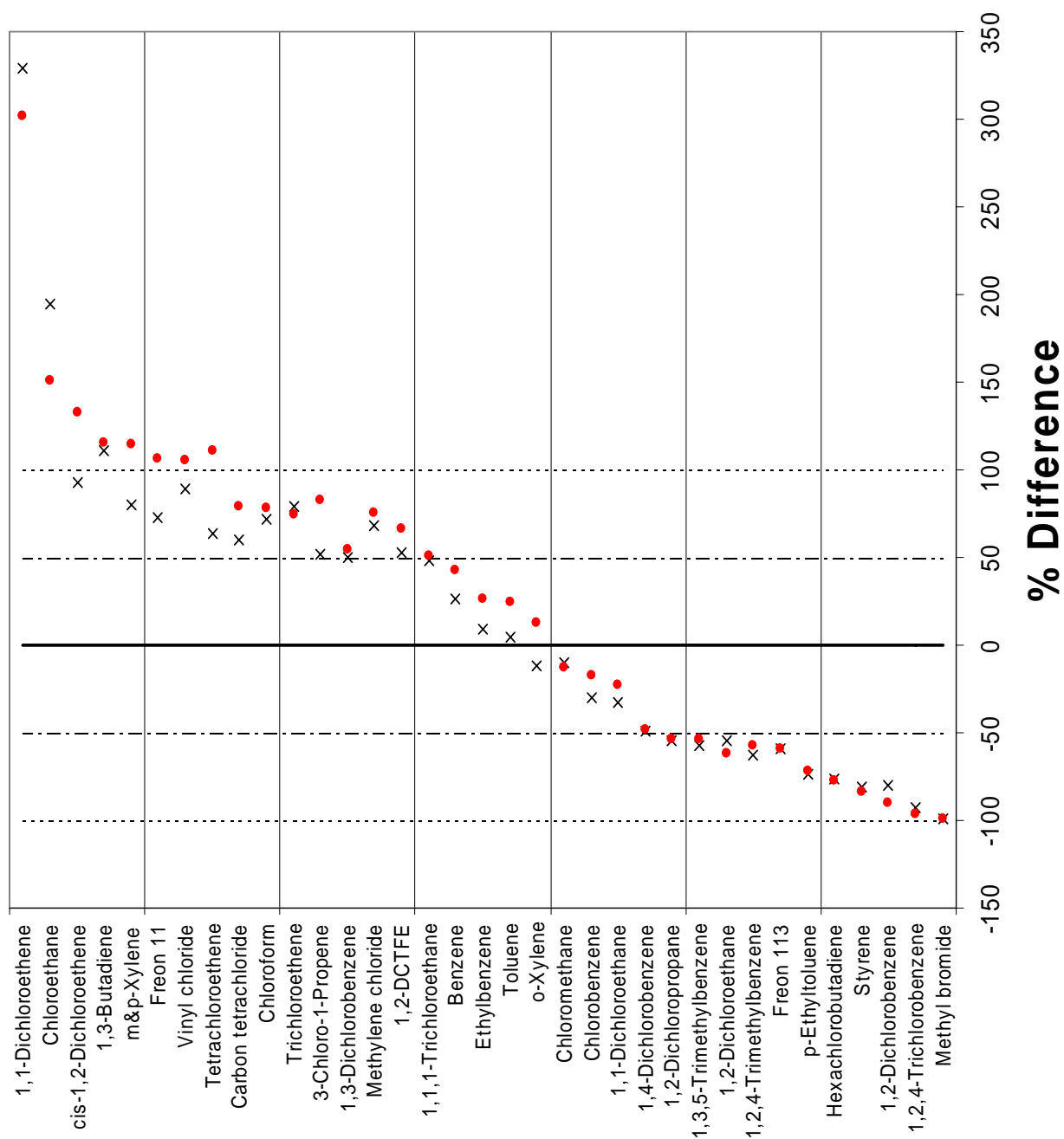


Figure 4-4: The average percent difference between the expected concentration and the concentration provided by the HAPSITE® for the 50 (x) and 200 (•) ppb tests.

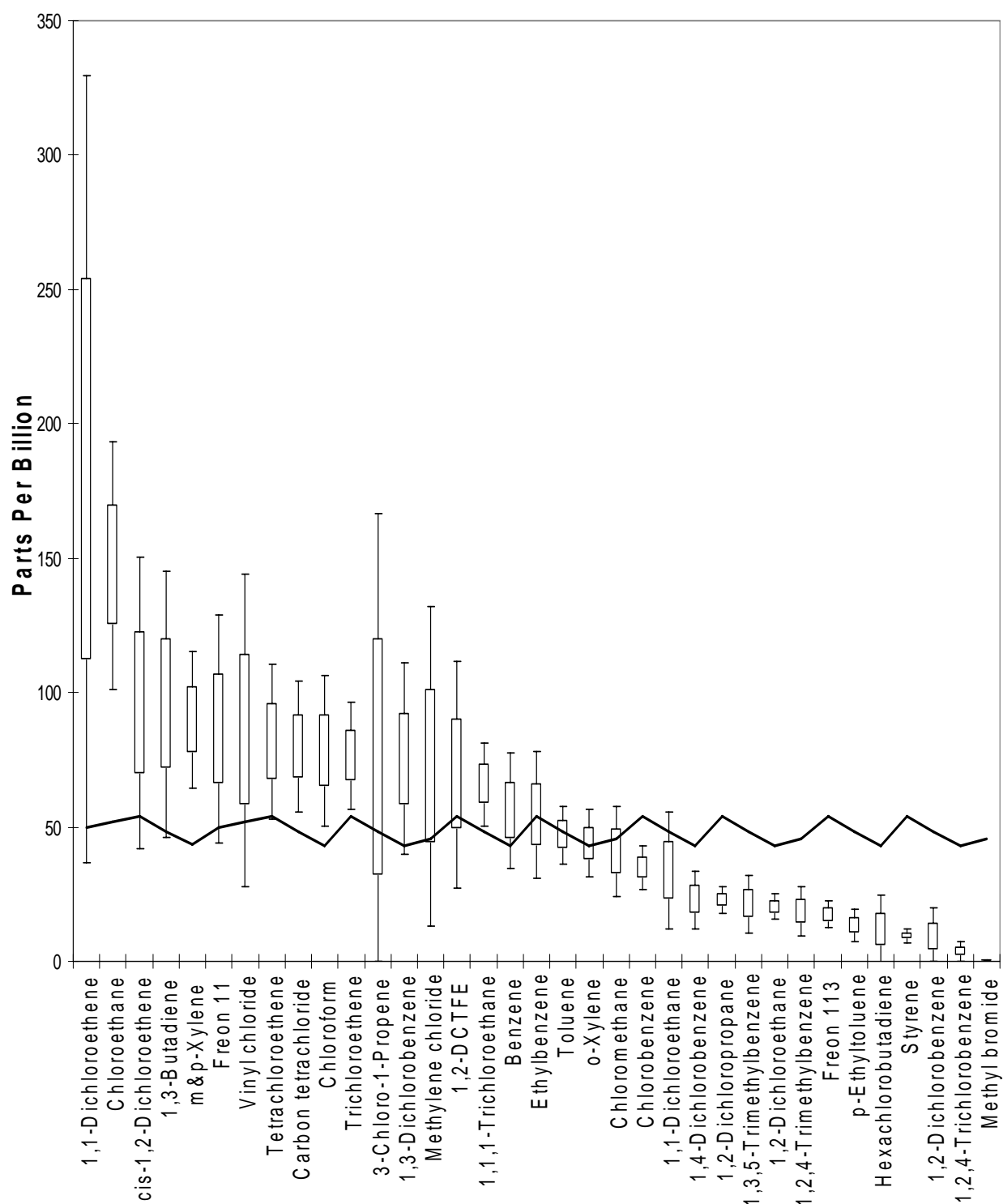


Figure 4-5: Tolerance Limits for each chemical at approximately 50 ppb. Box represents one standard deviation above and below the mean. Whiskers represent the tolerance interval. Solid line represents the expected concentration.

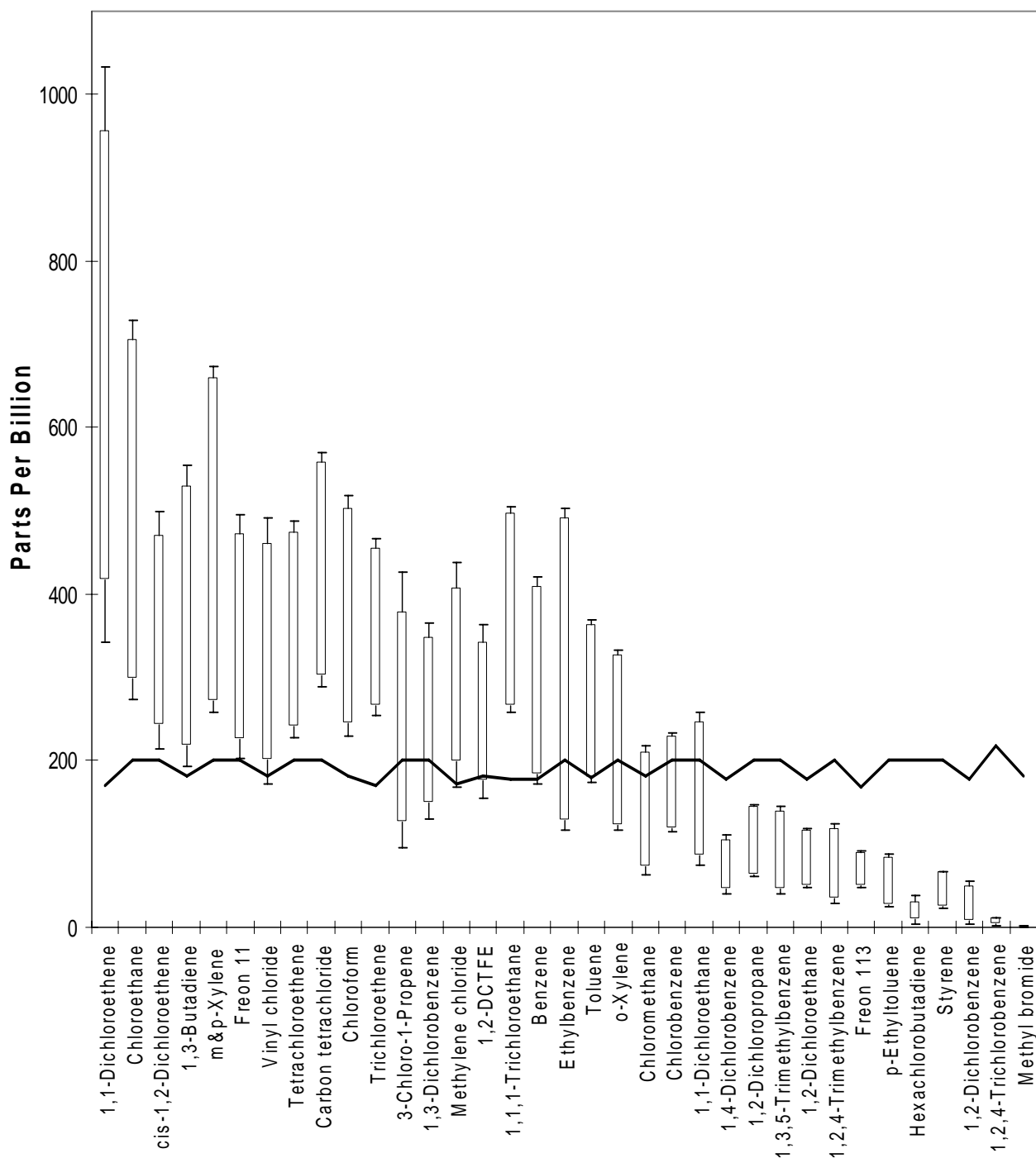


Figure 4-6: Tolerance Limits for each chemical at approximately 200 ppb. Box represents one standard deviation above and below the mean. Whiskers represent the tolerance interval. Solid line represents the expected concentration.

Location Analysis

Three different locations were used to conduct the tests on the 50 HAPSITE® instruments. At the three locations, the mean response for each chemical was determined and compared to the other two locations. The difference in the means for each chemical across the instruments at each location and each concentration are shown in Figures 4-7 and 4-8. Figures 4-7 and 4-8 show the comparison of the locations for each chemical at the 50 and 200 ppb, respectively. Data for the location analysis is found in Appendix C.

Figure 4-7 shows little difference between the Syracuse and San Antonio locations for most of the chemicals. The differences can be seen between the Ft. Leonard Wood data and the Syracuse and San Antonio data, with the Ft. Leonard Wood data being the highest in average response for 29 of the 35 chemicals. Figure 4-8 shows less of a difference between the three locations.

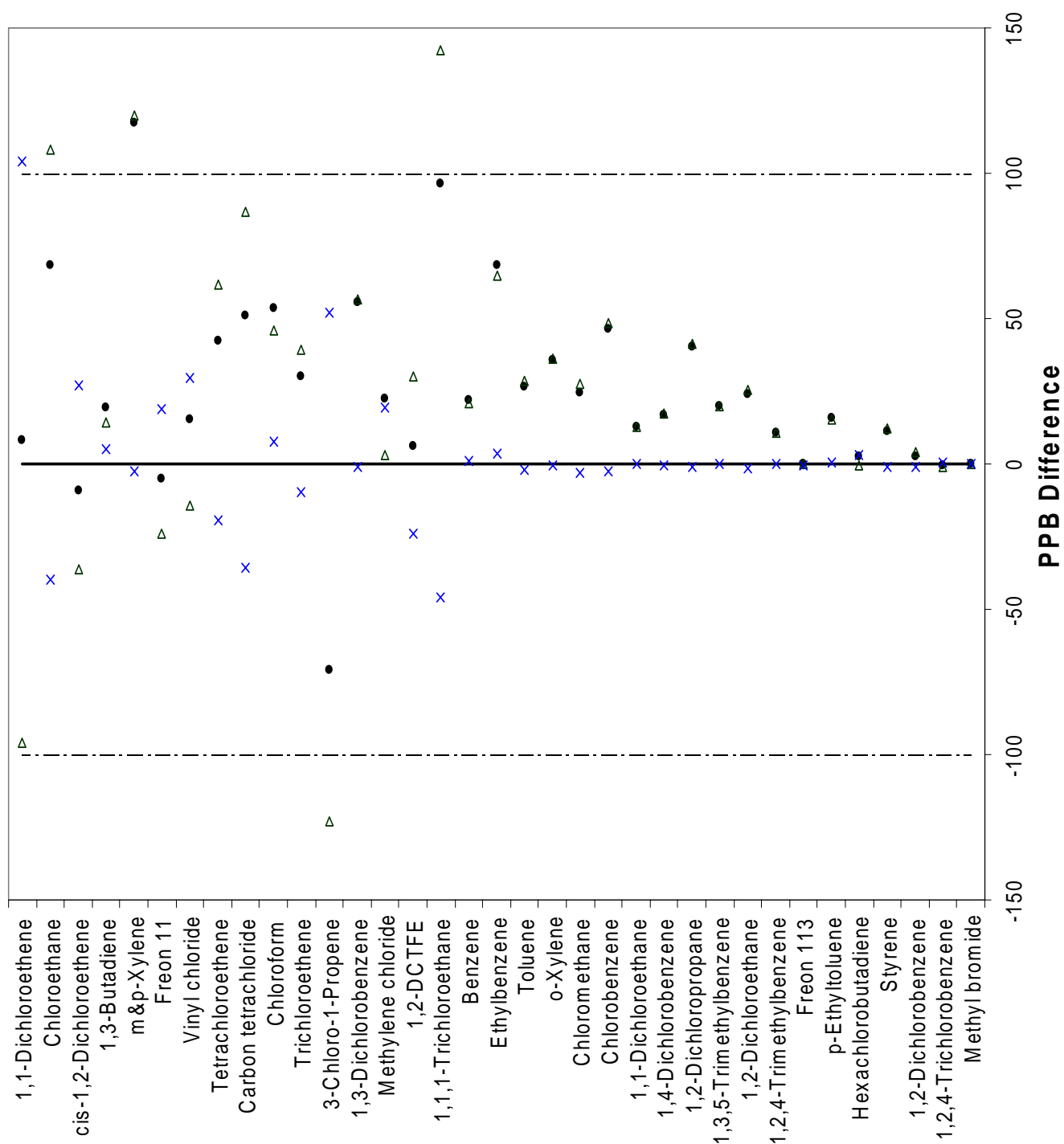


Figure 4-7: Difference between the means at 50 ppb from instruments at each location.
 (• = Ft. Leonard Wood-San Antonio, Δ = Ft. Leonard Wood-Syracuse, and
 x = Syracuse-San Antonio)

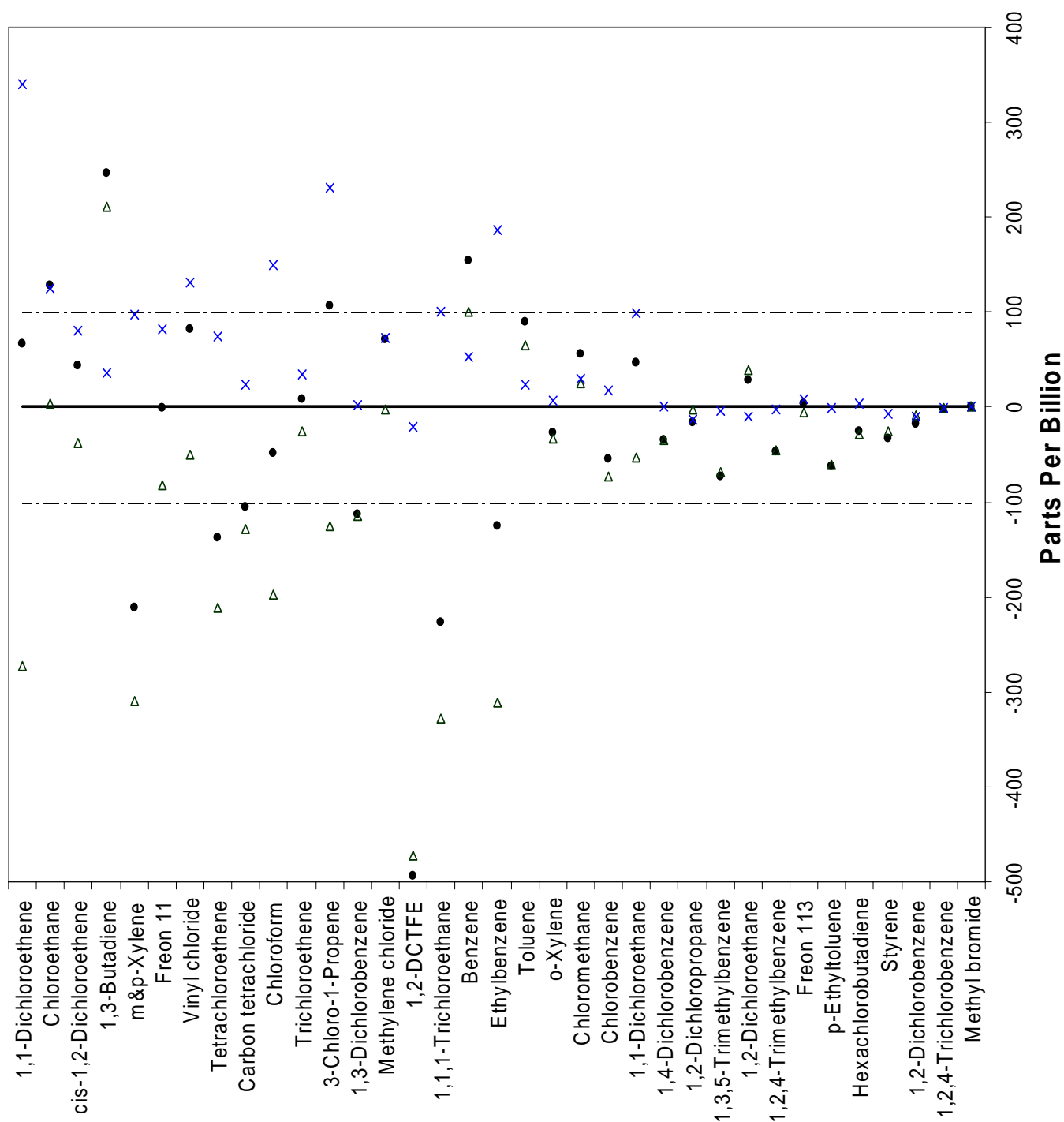


Figure 4-8: Difference between the means at 200 ppb from instruments at each location.

(• = Ft. Leonard Wood-San Antonio, Δ = Ft. Leonard Wood-Syracuse, and x = Syracuse-San Antonio)

The overall comparison of the means for the given locations and chemicals are provided in Table 4-1 and Table 4-2. This analysis investigated the significance of the influence that location has on the response of the HAPSITE® instruments. These tables show the overall difference between the three locations for all chemicals and a significance value for the difference. The mean response for each chemical at each location was compared. The total difference of all the mean values and the significance of the difference are shown in the tables. A difference is determined to be significant at a 0.05 level.

Table 4-1: Multiple Comparisons 50 ppb Location Analysis.
(FLW = Ft. Leonard Wood, SA = San Antonio, and Syr = Syracuse)

location	Mean Difference	Std. Error	p-value
FLW-SA	25.21(*)	6.39	.00
FLW-Syr	22.86(*)	6.39	.00
Syr-SA	2.35	6.39	.93

* The mean difference is significant at the 0.05 level.

Table 4-2: Multiple Comparisons 200 ppb Location Analysis
(FLW = Ft. Leonard Wood, SA = San Antonio, and Syr = Syracuse)

location	Mean Difference	Std. Error	p-value.
FLW-SA	-20.62	19.67	0.55
FLW -Syr	-76.05(*)	19.67	0.00
Syr-SA	55.43(*)	19.67	0.02

* The mean difference is significant at the 0.05 level.

Comparing the means for the chemicals from the 50 ppb runs showed that the Ft. Leonard Wood data was significantly higher than the other two locations. Also, San Antonio and Syracuse instruments showed very little statistical difference between their locations. Comparing the means for the chemicals from the 200 ppb runs showed that Syracuse instruments responded higher than the other two locations, also, San Antonio and Ft. Leonard

Wood instruments showed very little statistical difference between their locations. The only consistent statistical response by location, for both concentrations, was that the San Antonio instruments were always the lowest in total mean response. The trends were not consistent across all chemicals, thus location did not prove useful as a factor of variability.

Age Analysis

The age of the instrument was thought to be a potential cause for variability. The exact date of production for each instrument was not obtained during this study; however, a relative age could be gained by analyzing the serial numbers. The serial number provides the order in which the instruments were produced, providing a rough estimate of age. Figure 4-9 shows the distribution of instruments by serial number and by location. The instruments were ranked according to serial number and concentration estimate for the chemicals in the test cylinders. The rankings were analyzed using a Spearman Rank Correlation.

The results of the Spearman Rank Correlation for age of the instruments are provided in Table 4-3. This correlation showed a weak, negative correlation, which implies that as the age goes up the estimation of concentration goes down. Neither concentration was found to be significant to a 0.05 level. However, a weak trend suggests there may be some influence from age on the response of the HAPSITE® instruments.

Table 4-3: Spearman Rank Correlations for age and average instrument concentration estimate to 50 ppb and 200 ppb test mixtures (two-tailed t-test, $\alpha=0.05$)

Spearman Rank Correlations	correlation value	p-value
Age and 50ppb data	-0.2109	0.1548
Age and 200 ppb data	-0.2766	0.0518

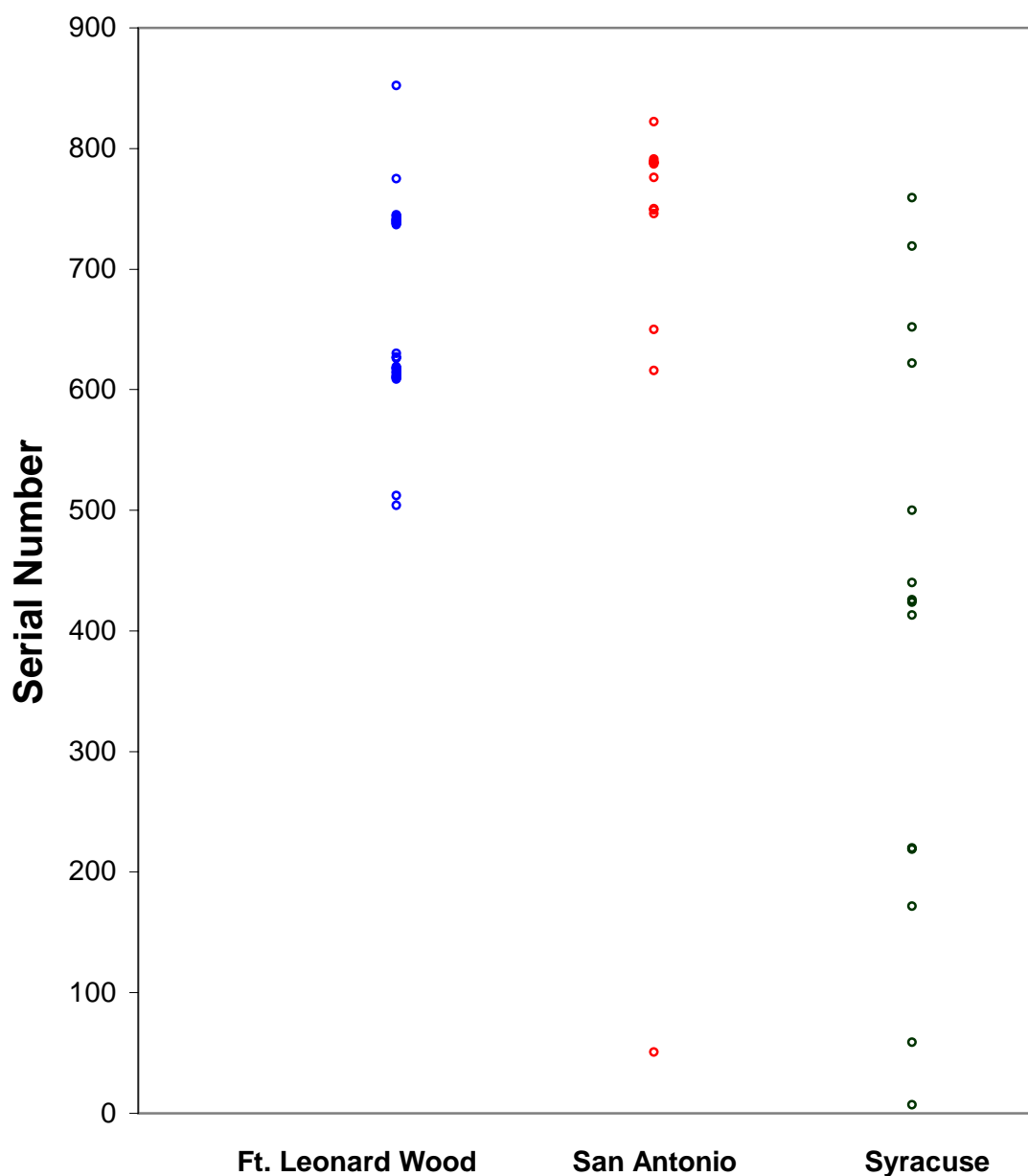


Figure 4-9: Display of the instruments by serial number and by location.

Sample Pump Flow Rate Analysis

Variations in the HAPSITE® internal air sample pump was also investigated. A BIOS® (Brandt Instruments, Prairieview, LA) DryCal DC-Lite flow meter, with low-flow cell, on the outlet port of the HAPSITE® during loopfill provided sample flow rate

information for the internal pump that draws the sample into the instrument. The internal air sample pump varied in a manner consistent with a reciprocating pump over the one-minute sample time, so ten flow measurements were taken on each instrument and averaged. The ten flow measurements took approximately one minute. The average measurement was used as the overall flow rate. Flow rates were compared to the average responses for each instrument across all chemicals.

The flow rates for the 50 instruments tested ranged from 49-123 ml/min. Only ten instruments had a flow rate within 5% of the expected flow rate of 100 ml/min. Figures 4-10 and 4-11 show the difference in range of recorded values from the HAPSITE® instruments with a flow rate of $100 \text{ ml/min} \pm 5\%$ and all of the HAPSITE® instruments tested. Comparing the %RSD for all 50 HAPSITE® instruments to the %RSD for the instruments with $100 \pm 5\%$ ml/min flow rate, the precision between instruments was improved from 25% to 16% for the 50 ppb runs and 41% to 17% for the 200ppb runs.

Taking the instruments tested, a correlation between sample flow rate and average instrument response was expected. The results from the Bivariate Normal Correlations are shown in Table 4-4. A positive correlation was found between sample flow rate and the average response of the instrument. A significant correlation was found at the 50 ppb concentration to the 0.05 level, while the 200 ppb was not significant to the same 0.05 level. This suggests that the lower concentration has a greater sensitivity to the sample pump flow rate.

Table 4-4: Bivariate Normal Correlation between sample flow rate and average instrument response, (two-tailed t-test, $\alpha=0.05$).

Bivariate Normal Correlations	Correlation value	p-value
Flow rate and 50 ppb	0.4217	0.0054
Flow rate and 200 ppb	0.2720	0.0814

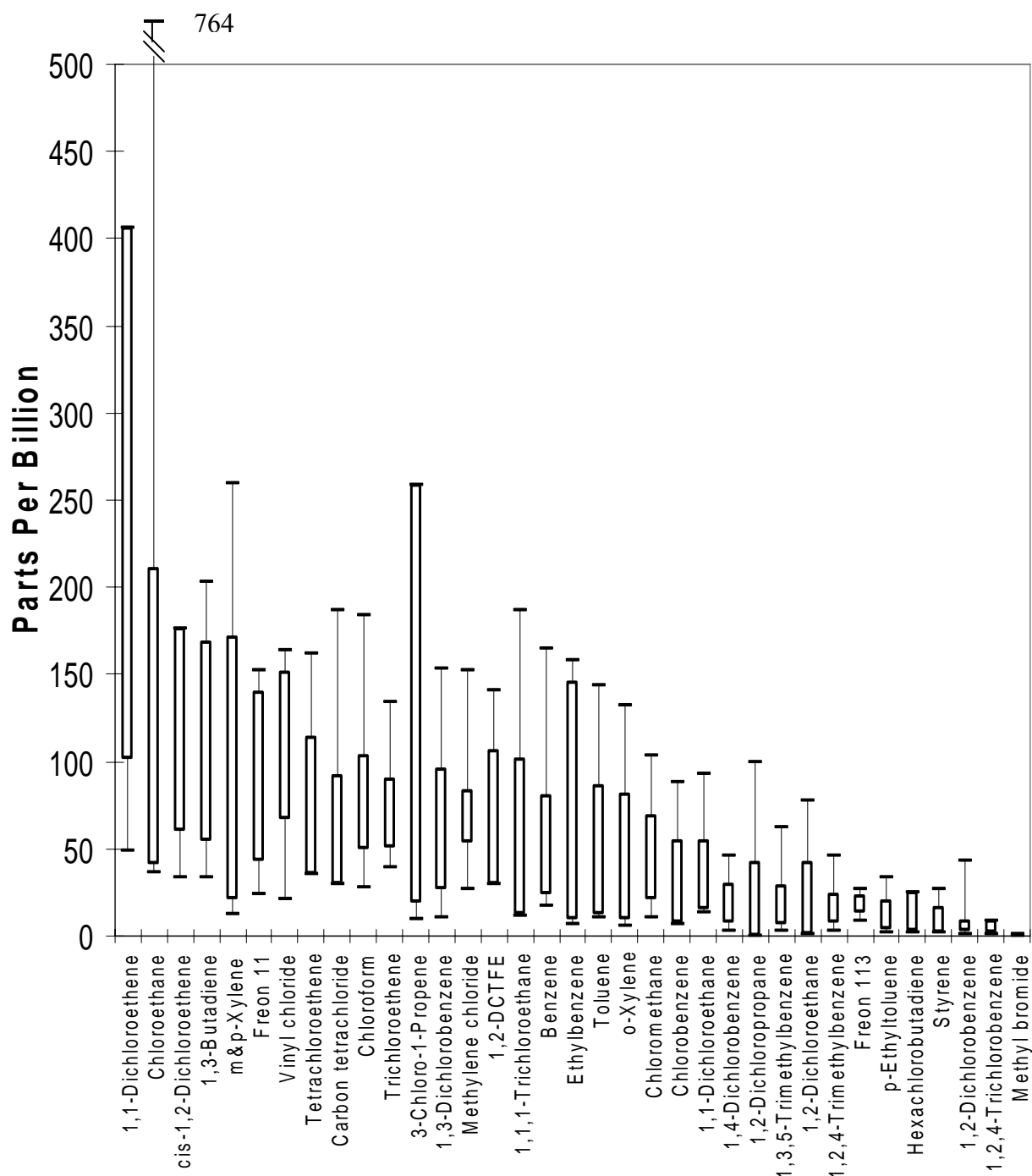


Figure 4-10: Comparison of the range of values seen when evaluating for flow rate. The "box" represents the range of values from HAPSITE® instruments with a flow rate of 100±5% ml/min. The "whiskers" represent the range of values from all HAPSITE® instruments tested.

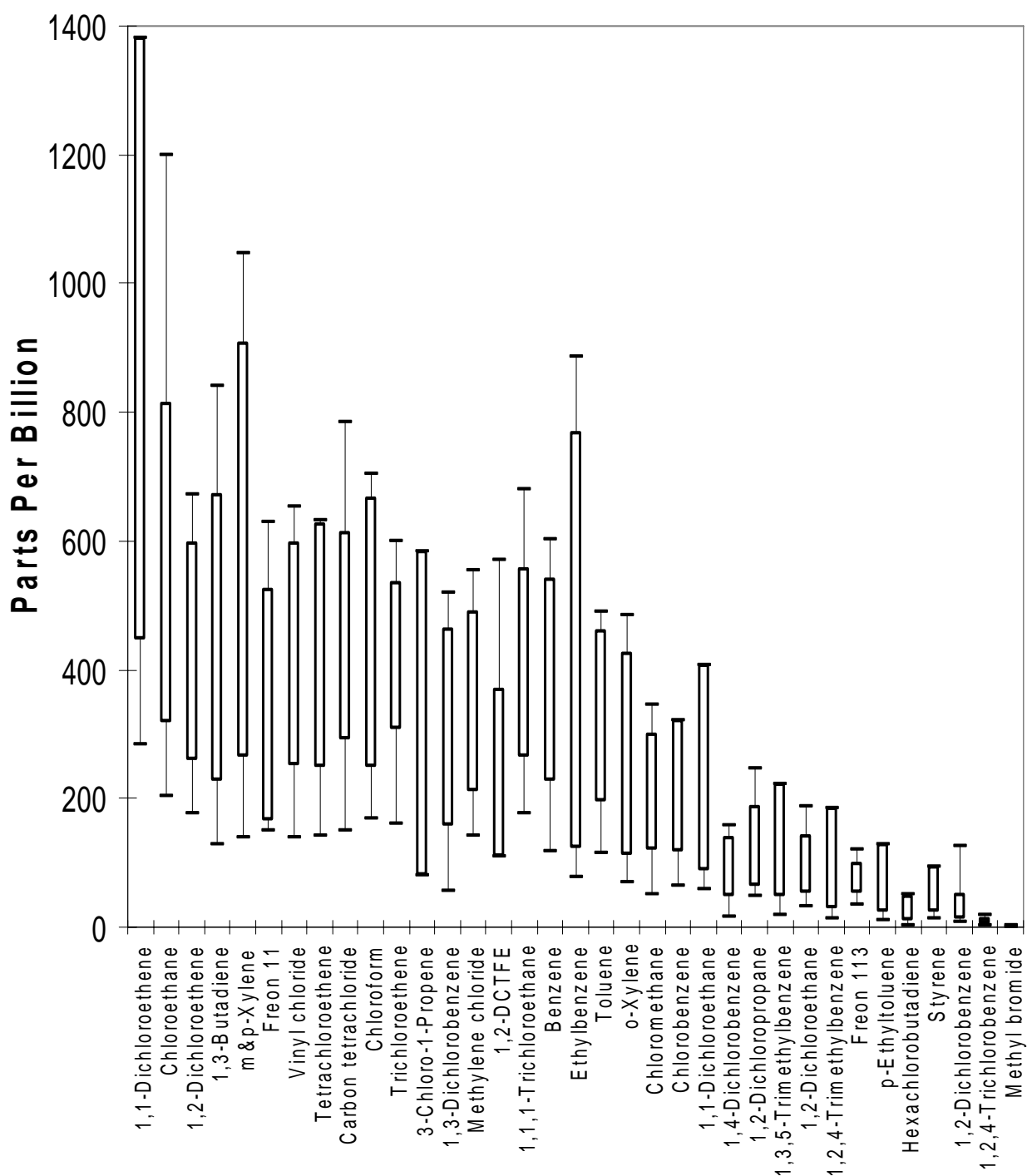


Figure 4-11: Comparison of the range of values recorded when evaluating for flow rate. The "box" represents the range of values from HAPSITE® instruments with a flow rate of 100±5% ml/min. The "whiskers" represent the range of values from all HAPSITE® instruments tested.

Cluster Analysis

Finally, a cluster analysis of the normalized data for concentration was performed using the SPSS computer program [SPSS® 7.5, 1997]. The normalization for concentration was necessary because the exact concentrations in the cylinders varied slightly from 50 and 200 ppb and to test for similarity the data had to be based on one common value per evaluation. Similarity is a comparison, of the mean and the standard deviation, of one chemical to all of the other chemicals. Chemicals are considered similar if the means and standard deviations meet the statistical criteria of 95% similar. All chemicals would respond similarly if the calibration curve for each chemical were a perfect representation of the mean for all instruments. Table 4-5 shows the clusters of chemicals that responded similarly at both concentrations. Cluster 1 contains the chemicals that had low estimated concentrations, while cluster 5 contains the chemicals that were consistently estimated higher than expected for both the 50 and 200 ppb tests.

Table 4-5: Clusters of chemicals responding similarly at 50 and 200 ppb concentrations.

Cluster 1	Cluster 2	Cluster 3
1,2,4-Trichlorobenzene (mCB)	Methylene chloride	o-Xylene
Hexachlorobutadiene	Benzene	Chloromethane (CA)
1,2-Dichloroethane (CA)	1,1,1-Trichloroethane (CA)	
1,3,5-Trimethylbenzene (mCB)	Carbon tetrachloride (CA)	Cluster 4
1,2,4-Trimethylbenzene (mCB)	Chloroform (CA)	cis-1,2-Dichloroethene
1,4-Dichlorobenzene (mCB)	Trichloroethene	Vinyl chloride
1,2-Dichloropropane (CA)	Tetrachloroethene	Freon 11
Freon 113		
p-Ethyltoluene		Cluster 5
Styrene		1,1-Dichloroethane (CA)
Methyl bromide		Chlorobenzene (CB)
1,2-Dichlorobenzene (mCB)		

Some general trends can be drawn from the clusters. Only 26 of the 35 chemicals in this test could be clustered. The instruments responded similarly for multi-chlorinated benzene compounds (mCB) however, 1,3-dichlorobenzene was an exception. The trimethylbenzene compounds showed similar responses across the instruments, while the o-xylene and m&p-xylene compounds were found to be dissimilar. Finally, chlorinated alkanes (CA) showed no similarities in instrument responses.

CHAPTER 5 - Conclusions

The purpose of this research was to determine the degree of variability and accuracy between the HAPSITE® portable GC-MS instruments using one common calibration curve for each chemical and a standard test mixture of 35 chemicals at two concentrations, 50 and 200 ppb. In addition to determining overall variability, this study evaluates major causes for the variability.

The results from this study have shown that there is variability between instrument responses when using the same calibration curve. A 25% RSD was found when comparing results from multiple reference laboratories testing the same sample, using laboratory standard GC-MS [EPA, 2001]. The %RSD for the HAPSITE® instruments in this study had an average of 25% and 41% for the 50 and 200 ppb tests, respectively.

The reasonable precision with wide ranging accuracy (-99 to +323) shown in this study suggests that using the calibration curves from the MRI study may be the primary cause of inaccuracy. The data from this study may be used to find a more accurate calibration curve, because the data from the 50 instruments used in this study can be re-analyzed using different calibration curves. A single curve from one instrument that responds at the mean of the studied instruments would provide the best possible curve to be used on all instruments.

Some trends were found that influenced the variability of these instruments, the most prominent being the flow rate of the sample pump. Comparisons of the results from a specified flow rate of 100 ± 5 ml/min to the results across the entire range of flow rates showed a significant reduction in variability, bringing the %RSD down to 16% for 50 ppb samples and 17% for the 200 ppb samples, from 25% and 41% respectively. This compares very well with 25% found in the EPA (2001) study of reference laboratories. This shows that

if the flow rate of the sample pump was held to the 100 ml/min expected flow, the overall variability across all HAPSITE® instruments would be reduced.

The lack of accuracy found during this study suggests that an investigation of the calibration curves for these chemicals may be needed. The tolerance intervals for a given chemical should be within 10% of the expected value if an accurate calibration curve is used and represents the mean instrument response. A consistent flow rate for every HAPSITE® would also help the instrument be more accurate through the elimination of a known factor that affects variability.

No conclusion can be made on the influence that location had on response. The locations had significant, but inconsistent differences at the two concentrations. The San Antonio instruments showed the lowest response at both concentrations compared to Ft. Leonard Wood and Syracuse Instruments. But the order of highest to lowest responses by location was not consistent between the results for the two concentrations. In order to determine if some component of geographical location has an impact on the overall response of the instrument, more locations need to be studied.

The age of the instruments did not show a significant impact on the overall response. This may be due to using the serial numbers as the measure of age. A better parameter to investigate would be the time since last maintenance or manufacturer calibration for an instrument. This would provide a better indication of changes over time for the response of an instrument.

In order to provide the best information during a response, a calibration curve needs to be generated that closely represents the median of instrument responses with a control for the sample pump. The flow rate of the sample pump should be run at the 100 ± 5 ml/min or have

the internal software obtain the flow rate information and adjust the quantification report to provide a more precise concentration estimate.

Finally, a program should be generated that sends a specific concentration of known chemicals to the field operators to run and quantify on the HAPSITE®. It would be best to track the responses of an instrument against the data from the laboratory preparation of the concentration at different times. This will provide a trend log for the operator for use in quantification scenarios for their instrument. The trending of the instrument's responses provides the operator with the knowledge of their specific instrument and how it generally responds. This knowledge will help operators provide a response to on-scene commanders with greater accuracy.

Study Limitations or Further Research Opportunities

This study did not look at the effects of different tuning parameters on the response and variability found within the study group. A standard tune uses only three tuning parameters where this research used seven tuning parameters. The information on the effects that different tunes have on response would aid the training of operators and optimize the ability of personnel to use this instrument to its full capacity. The adjustment of column pressure to ensure the proper retention time of the internal standards would also need to be added to the training curriculum, so the response personnel can adjust the operating conditions of the HAPSITE® to produce the quantitation report.

Another limitation was that the concentration inside the compressed gas cylinders were not independently tested. The sampling of the test configuration could have helped determine what results were different than expected because of the test configuration and not

attributable to the instrument. However, PortaGas assures $\pm 10\%$ of the expected concentration for six months.

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Appendix A: Concentration estimates, provided by PortaGas, for test chemicals in the compressed gas cylinders at for 50 parts per billion test

Mol Wt = Molecular weight, Conc = expected concentration, min and max = upper and lower bound of concentration error

Chemical	Mol.Wt.	Conc (ppb)	min	max
Chloromethane	50.5	46	41	50
Vinyl chloride	62.5	46	41	50
Methyl bromide	95	46	41	50
Chloroethane	64.5	50	45	55
Freon 11	137.36	50	45	55
Freon 113	187.4	42	38	47
Trichloroethene	131.4	43	38	47
p-Ethyltoluene	121.16	50	45	55
cis-1,2-Dichloroethene	97	50	45	55
1,1-Dichloroethene	97	43	38	47
Methylene chloride	84.9	43	39	48
1,1-Dichloroethane	99	50	45	55
Chloroform	119.4	46	41	50
1,2-Dichloroethane	99	45	40	49
1,1,1-Trichloroethane	133.4	45	40	49
Benzene	78.1	45	40	49
Carbon tetrachloride	153.8	50	45	55
1,2-Dichloropropane	112.978	50	45	55
Toluene	92.1	45	41	50
Tetrachloroethene	165.8	50	45	55
Chlorobenzene	112.6	50	45	55
Ethylbenzene	106.2	50	45	55
m&p-Xylene	106.2	50	45	55
Styrene	104.2	50	45	55
o-Xylene	106.2	50	45	55
1,3,5-Trimethylbenzene	120.2	50	45	55
1,2,4-Trimethylbenzene	120.2	50	45	55
1,3-Dichlorobenzene	147	50	45	55
1,4-Dichlorobenzene	147	45	40	49
1,2-Dichlorobenzene	147	45	40	49
1,2,4-Trichlorobenzene	181.4	55	49	60
Hexachlorobutadiene	260.7	50	45	55
1,2-Dichlorotetrafluoroethane	170.9	46	41	50
1,3-Butadiene	54.1	46	41	50
3-Chloro-1-Propene	89.5	50	45	55

Appendix A: Concentration estimates, provided by PortaGas, for test chemicals in the compressed gas cylinders at 200 ppb

Chemical	Mol.Wt.	Conc (ppb)	min	max
Chloromethane	50.5	182	164	200
Vinyl chloride	62.5	182	164	200
Methyl bromide	95	182	164	200
Chloroethane	64.5	200	180	220
Freon 11	137.36	200	180	220
Freon 113	187.4	169	152	186
Trichloroethene	131.4	171	154	188
p-Ethyltoluene	121.16	200	180	220
cis-1,2-Dichloroethene	97	200	180	220
1,1-Dichloroethene	97	171	154	188
Methylene chloride	84.9	173	155	190
1,1-Dichloroethane	99	200	180	220
Chloroform	119.4	182	164	200
1,2-Dichloroethane	99	178	160	196
1,1,1-Trichloroethane	133.4	178	160	196
Benzene	78.1	178	160	196
Carbon tetrachloride	153.8	200	180	220
1,2-Dichloropropane	112.978	200	180	220
Toluene	92.1	180	162	198
Tetrachloroethene	165.8	200	180	220
Chlorobenzene	112.6	200	180	220
Ethylbenzene	106.2	200	180	220
m&p-Xylene	106.2	200	180	220
Styrene	104.2	200	180	220
o-Xylene	106.2	200	180	220
1,3,5-Trimethylbenzene	120.2	200	180	220
1,2,4-Trimethylbenzene	120.2	200	180	220
1,3-Dichlorobenzene	147	200	180	220
1,4-Dichlorobenzene	147	178	160	196
1,2-Dichlorobenzene	147	178	160	196
1,2,4-Trichlorobenzene	181.4	218	196	240
Hexachlorobutadiene	260.7	200	180	220
1,2-Dichlorotetrafluoroethane	170.9	182	164	200
1,3-Butadiene	54.1	182	164	200
3-Chloro-1-Propene	89.5	200	180	220

Appendix B: Tolerance Limits for 50 ppb and 200 ppb by Chemical

Average is the mean concentration estimate for the 50 HAPSITE® instruments

%RSD is the relative standard deviation for the 50 HAPSITE® instruments

Tolerance limit is the range that 95% of all instruments are predicted to respond

chemical	50 parts per billion		95% Tolerance Limits		200 parts per billion		95% Tolerance Limits	
	average	%RSD	lower	upper	average	%RSD	lower	upper
Chloromethane	41	20	24	58	141	49	0	283
Vinyl chloride	86	33	28	144	332	39	63	600
Methyl bromide	0	55	0	1	1	38	0	3
Chloroethane	147	15	101	193	502	41	80	924
Freon 11	86	24	44	129	349	36	93	605
Freon 113	17	14	12	22	70	29	29	111
Trichloroethene	76	13	57	96	361	26	164	558
p-Ethyltoluene	13	22	7	20	56	51	0	115
cis-1,2-Dichloroethene	96	27	42	151	356	32	121	592
1,1-Dichloroethene	183	39	37	330	687	39	131	1244
Methylene chloride	73	40	13	132	304	34	88	519
1,1-Dichloroethane	34	31	12	56	166	49	0	333
Chloroform	78	17	51	106	374	35	106	642
1,2-Dichloroethane	20	11	16	25	83	40	15	151
1,1,1-Trichloroethane	66	11	50	81	382	30	143	620
Benzene	56	19	35	78	296	38	64	529
Carbon tetrachloride	80	15	55	104	430	30	166	694
1,2-Dichloropropane	23	10	18	28	104	39	20	189
Toluene	47	11	36	58	271	34	83	460
Tetrachloroethene	82	17	53	110	358	32	118	597
Chlorobenzene	35	11	27	43	174	32	61	287
Ethylbenzene	54	21	31	78	309	59	0	684
m&p-Xylene	90	14	65	115	466	42	65	868
Styrene	9	13	7	12	45	46	2	89
o-Xylene	44	14	31	57	225	45	14	435
1,3,5-Trimethylbenzene	21	24	11	32	92	51	0	190
1,2,4-Trimethylbenzene	18	24	9	28	76	55	0	164
1,3-Dichlorobenzene	75	23	40	111	248	40	44	453
1,4-Dichlorobenzene	23	23	12	34	75	40	13	137
1,2-Dichlorobenzene	9	57	0	20	29	73	0	73
1,2,4-Trichlorobenzene	4	46	0	7	7	51	0	14
Hexachlorobutadiene	12	50	0	25	20	54	0	43
1,2-Dichlorotetrafluoroethane	69	29	27	112	260	32	88	431
1,3-Butadiene	96	25	46	145	374	41	54	695
3-Chloro-1-Propene	76	58	0	166	253	50	0	513

Appendix C: Difference in the Mean Response by Location for 50 ppb Samples

Compares the mean value at each location and subtracts from the mean at another

Chemical	FLW	SA	Syr	FLW-SA	FLW-Syr	Syr-SA
1,1-Dichloroethene	189	181	285	8	-96	104
Chloroethane	190	122	82	68	108	-40
cis-1,2-Dichloroethene	85	95	122	-9	-36	27
1,3-Butadiene	66	47	52	19	14	5
m&p-Xylene	150	32	30	118	120	-2
Freon 11	79	85	103	-5	-24	19
Vinyl chloride	87	71	101	15	-14	30
Tetrachloroethene	145	103	84	42	62	-19
Carbon tetrachloride	142	91	55	51	87	-36
Chloroform	119	65	73	54	46	8
Trichloroethene	93	63	54	30	39	-9
3-Chloro-1-Propene	29	100	152	-71	-123	52
1,3-Dichlorobenzene	103	47	46	56	57	-1
Methylene chloride	68	46	65	23	3	19
1,2-DCTFE	228	222	198	6	30	-24
1,1,1-Trichloroethane	171	74	28	97	142	-46
Benzene	39	17	18	22	21	1
Ethylbenzene	87	19	22	69	65	4
Toluene	37	10	8	27	29	-2
o-Xylene	45	10	9	36	36	-1
Chloromethane	48	23	20	25	28	-3
Chlorobenzene	60	14	12	46	49	-2
1,1-Dichloroethane	34	21	21	13	13	0
1,4-Dichlorobenzene	31	14	14	17	17	0
1,2-Dichloropropane	43	3	2	40	42	-1
1,3,5-Trimethylbenzene	31	11	11	20	20	0
1,2-Dichloroethane	27	3	2	24	26	-2
1,2,4-Trimethylbenzene	20	9	10	11	11	0
Freon 113	17	17	17	0	0	0
p-Ethyltoluene	24	8	9	16	15	0
Hexachlorobutadiene	19	16	19	3	-1	3
Styrene	15	4	3	11	12	-1
1,2-Dichlorobenzene	9	6	5	3	4	-1
1,2,4-Trichlorobenzene	2	3	3	0	-1	1
Methyl bromide	0	0	0	0	0	0

FLW = Ft. Leonard Wood, MO

SA = San Antonio, TX

Syr = Syracuse, NY

Appendix C: Difference in the Mean Response by Location for 200 ppb Samples

Chemical	FLW	SA	Syr	FLW-SA	FLW-Syr	Syr-SA
1,1-Dichloroethene	679	612	951	67	-273	339
Chloroethane	534	405	530	129	4	125
cis-1,2-Dichloroethene	356	313	394	43	-37	81
1,3-Butadiene	425	179	215	246	210	36
m&p-Xylene	335	546	644	-211	-309	98
Freon 11	326	327	408	-1	-83	81
Vinyl chloride	337	256	387	82	-50	132
Tetrachloroethene	354	492	566	-138	-212	74
Carbon tetrachloride	447	552	575	-105	-128	23
Chloroform	350	398	547	-48	-197	149
Trichloroethene	356	347	381	9	-26	35
3-Chloro-1-Propene	243	137	369	106	-126	232
1,3-Dichlorobenzene	189	302	304	-113	-114	1
Methylene chloride	297	227	299	71	-2	72
1,2-DCTFE	279	774	752	-494	-473	-22
1,1,1-Trichloroethane	378	604	705	-227	-327	101
Benzene	283	128	181	154	101	53
Ethylbenzene	192	317	503	-125	-311	186
Toluene	229	139	164	89	65	24
o-Xylene	154	180	187	-26	-33	7
Chloromethane	161	105	135	57	26	31
Chlorobenzene	147	202	220	-55	-73	18
1,1-Dichloroethane	146	100	199	47	-52	99
1,4-Dichlorobenzene	57	92	92	-34	-35	0
1,2-Dichloropropane	100	117	103	-17	-3	-14
1,3,5-Trimethylbenzene	56	128	124	-73	-68	-4
1,2-Dichloroethane	91	62	52	28	39	-10
1,2,4-Trimethylbenzene	42	90	87	-48	-45	-3
Freon 113	69	65	74	4	-5	9
p-Ethyltoluene	34	96	96	-62	-61	0
Hexachlorobutadiene	13	38	42	-25	-28	3
Styrene	30	62	56	-32	-26	-7
1,2-Dichlorobenzene	19	37	27	-18	-8	-9
1,2,4-Trichlorobenzene	5	7	6	-2	-1	-1
Methyl bromide	2	1	1	1	0	0

FLW = Ft. Leonard Wood, MO

SA = San Antonio, TX

Syr = Syracuse, NY

Appendix D: Additional Hapsite Data

NEG Pump and Ion Pump hours document the length of time the respective pumps have been in use

Serial #	Location	NEG Pump (hrs)	Ion Pump (hrs)	Serial #	Location	NEG Pump (hrs)	Ion Pump (hrs)
7	Syr	50.5	4676	627	FLW	47.6	390
51	SA	43.6	1598	630	FLW	50.5	419
59	Syr	29.8	1783	650	SA	35.9	161
172	Syr	55.5	531	652	Syr	30	148
219	Syr	0.7	214	719	Syr	25.3	173
220	Syr	5.9	729	737	FLW	23.9	183
413	Syr	24	319	738	FLW	None Recorded	
424	Syr	5	1070	739	FLW	9	286
426	Syr	113.3	1458	740	FLW	56.4	375
440	Syr	55	975	741	FLW	51.6	333
500	Syr	91.7	1809	742	FLW	36.1	319
504	FLW	42.4	600	744	FLW	57.1	374
512	FLW	53.7	264	745	FLW	54	396
609	FLW	55.7	335	746	SA	34.6	141
610	FLW	52.5	299	749	SA	36.8	150
611	FLW	48.2	397	750	SA	40.3	166
612	FLW	56.2	498	759	Syr	15.4	771
614	FLW	69.4	619	775	FLW	34.4	227
615	FLW	78.1	684	776	SA	None Recorded	
616	SA	9.1	508	787	SA	14.3	126
617	FLW	47.6	332	788	SA	14.2	129
618	FLW	65.5	593	789	SA	18.3	127
619	FLW	73.8	441	791	SA	21.4	150
622	Syr	23	85	822	SA	1.6	17
626	FLW	33	311	852	FLW	6.8	55

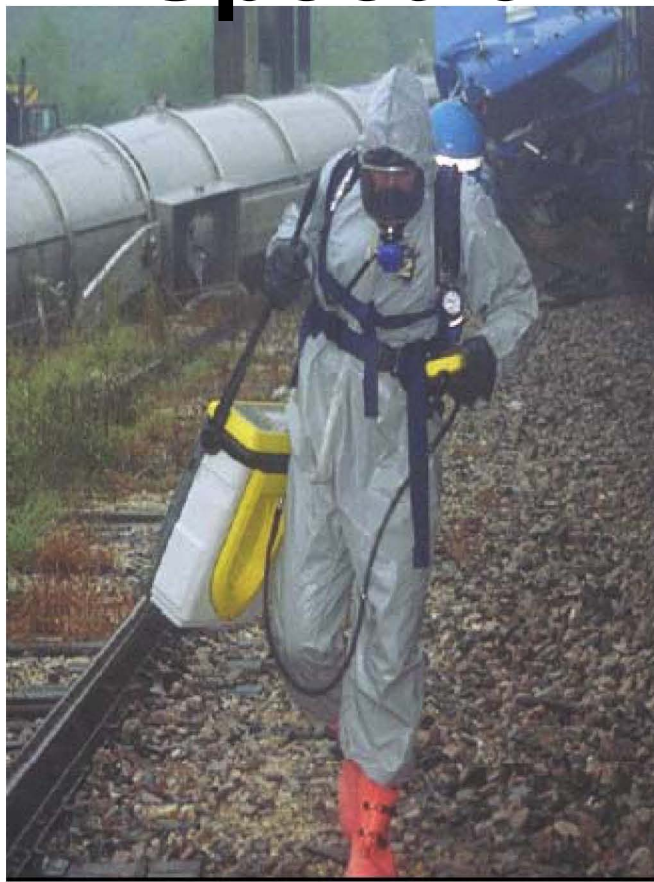
FLW = Ft. Leonard Wood, MO

SA = San Antonio, TX

Syr = Syracuse, NY



Hapsite Gas Chromatograph/Mass Spectrometer (GC-MS) Variability Assessment



Michael A. Skinner, Capt, USAF



Purpose

To determine if it is feasible to use one shared calibration curve on all Hapsite instruments for field estimation of chemical concentration



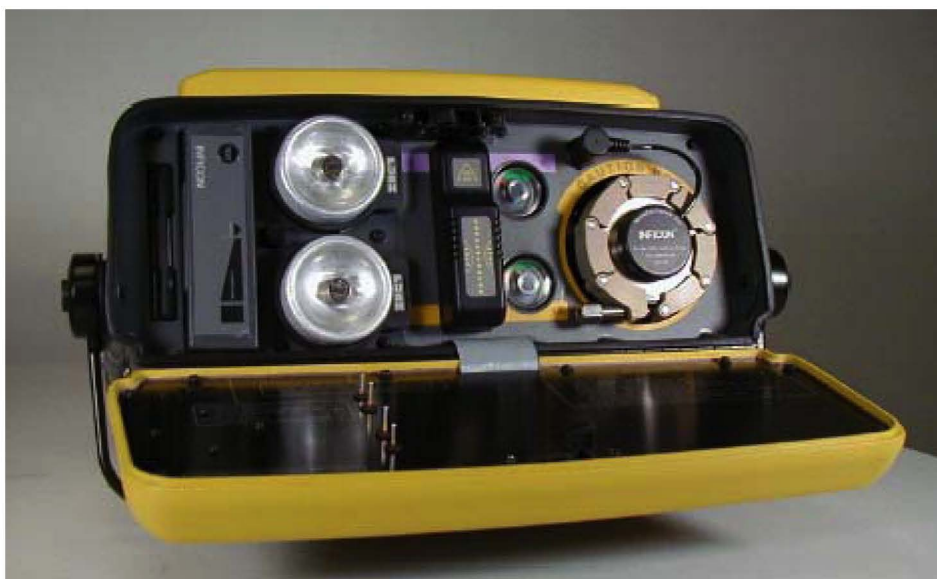
Outline

- **Background**
- **Methods**
- **Statistical Analysis**
- **Results**
- **Limitations**
- **Conclusion**
- **Recommendations**



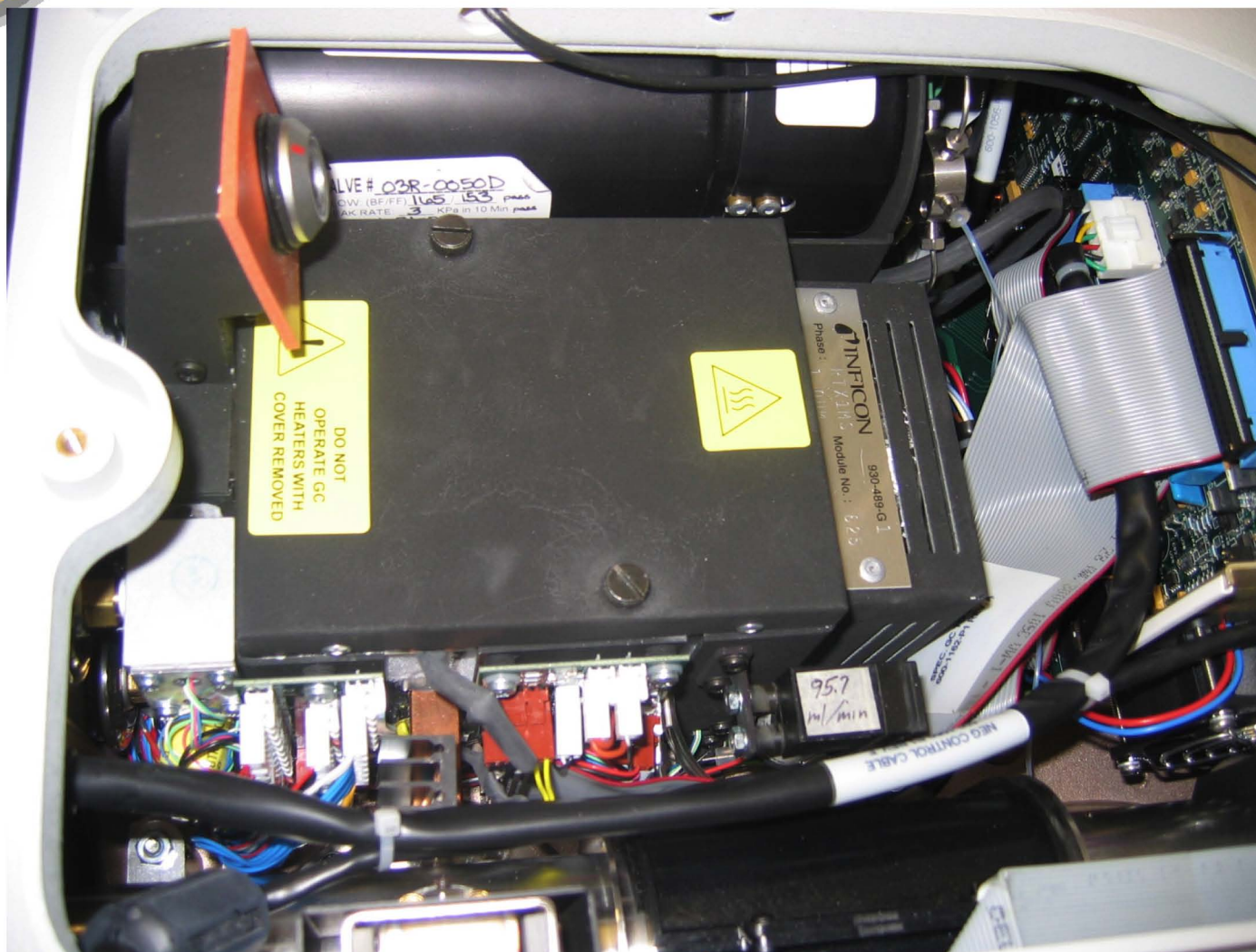
Inficon[®] HAPSITE[®]

- **Man-Portable GC-MS**
 - 18 in. x 17 in. x 7 in.
 - 35 lbs



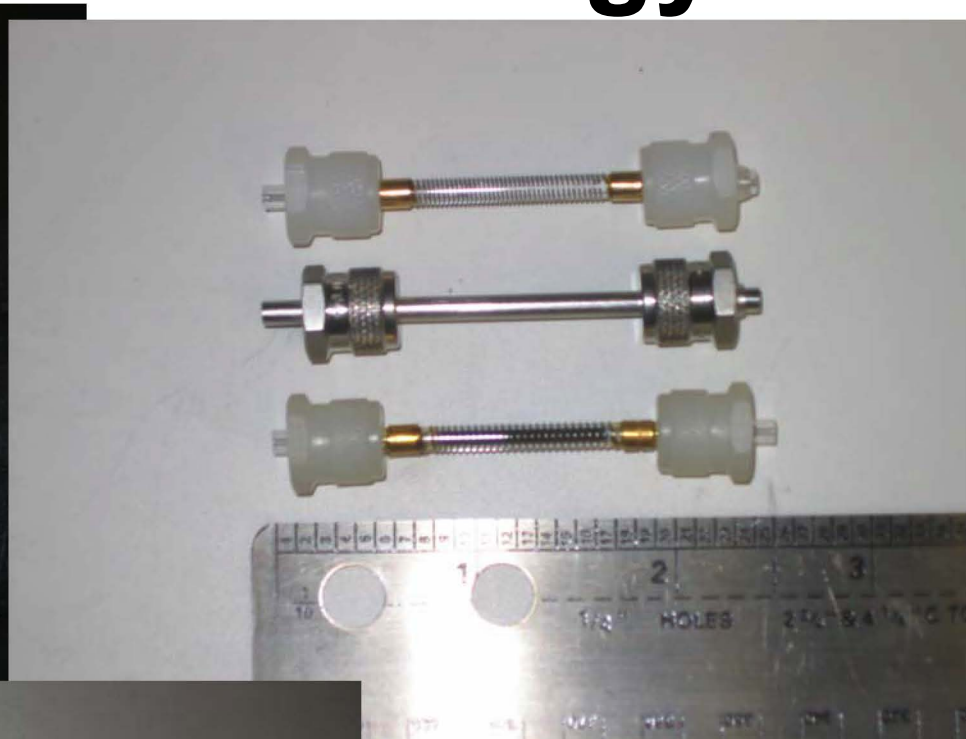


HAPSITE[®] Technology





HAPSITE[®] Technology





Users

- **Air Force - Bioenvironmental Engineers**
- **Navy – Environmental and Preventive Medicine Units**
- **Army (Guard) – Civil Support Teams**
- **Marines – Chemical, Biological Immediate Response Force**
- **Non DoD users**
 - Fire Departments
 - Private Industry



Uses

- **Emergency Response**
 - Unknown chemical Identification
 - Possible field concentration estimate
- **Traditional Industrial Hygiene**
- **Environmental Health Surveillance**



Research Question

**How much variability exists between
Hapsite instruments and what are the
major sources of variability?**



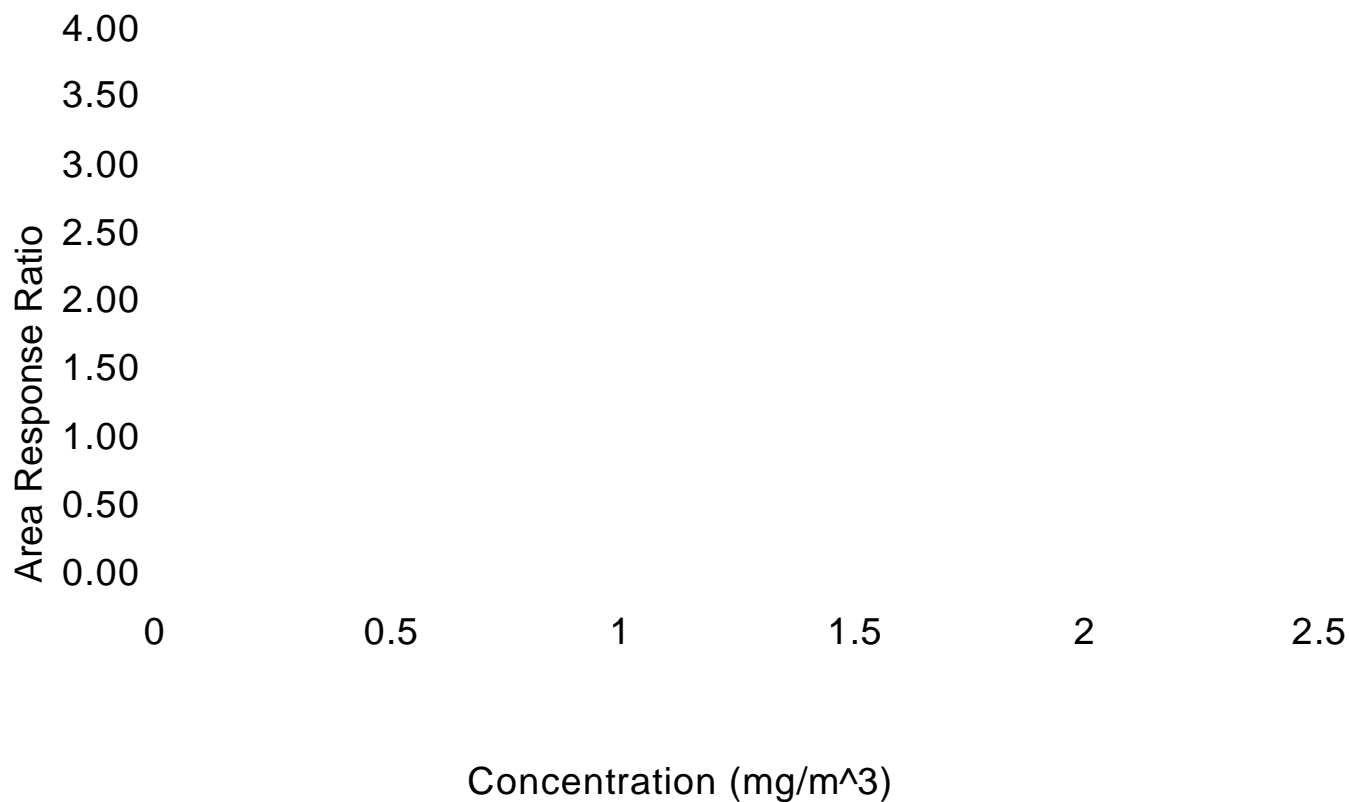
Specific Aims

- **Test 50 instruments against 35 chemicals at 50 and 200 ppb**
- **Develop 95 percent tolerance limit for each chemical to be used on all fielded instruments**
- **Identify trends in instrument response by chemical compound, instrument age, location, or other factors**



Calibration Curves

Navy TIC Calibration Curve - Freon 113





Test Set-up





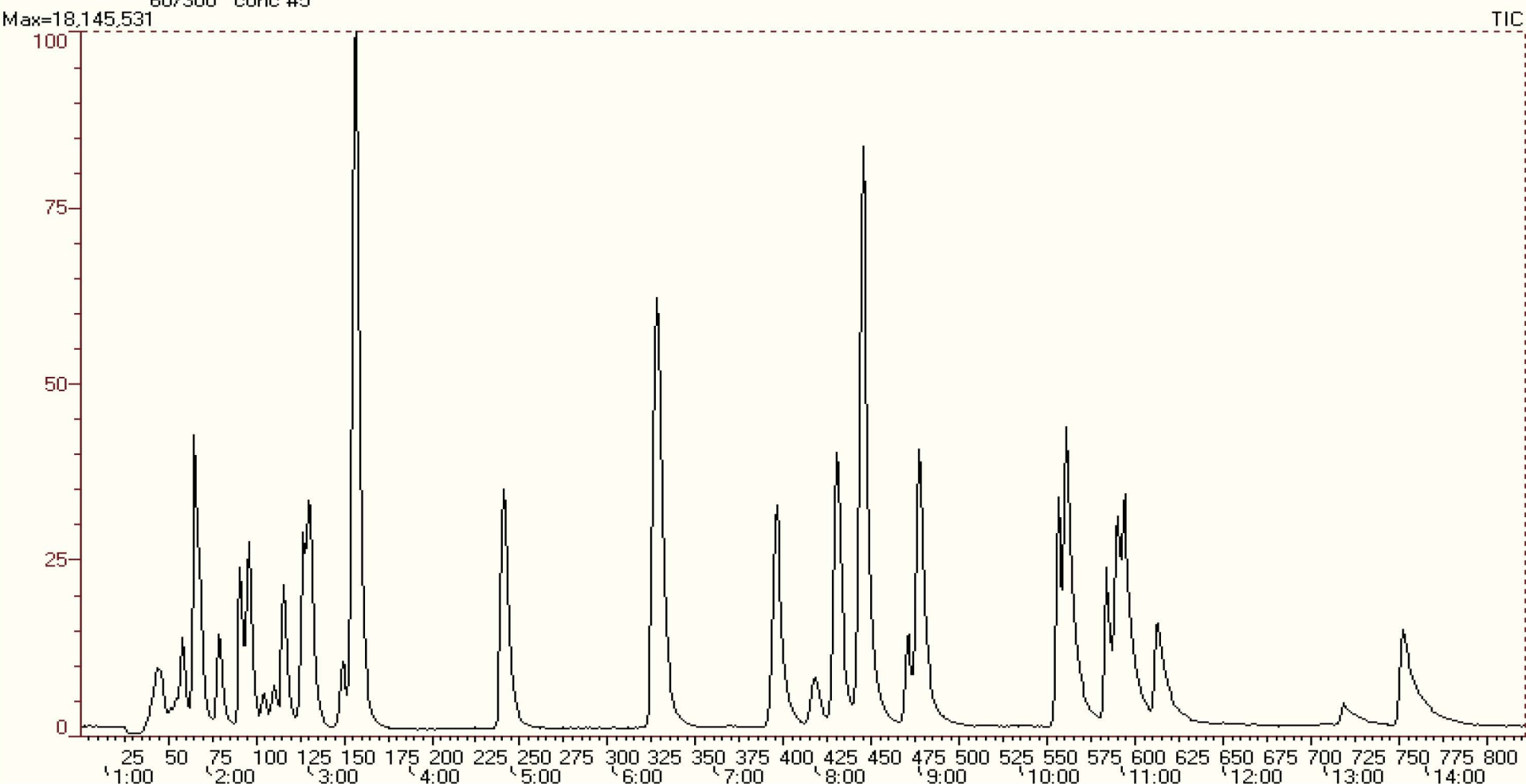


Sample Test

PACQ for HAPSITE - [Chro: 77608 Scans 1 to 822]
File Plots Chro Modes Options Libraries Window Help

Chromatogram: c:\data\776usaf\77608 Scans 1 to 822
Run: 08/30/04 at 19:51:44 RTime 0:46.05 to 14:59.09
200ppb-3 AFIOH
60/300 conc #5

Max=18,145,531



Chromatogram <PLOT MODE>: [LMB/Space] Select Spectra: +[Shift] Bkgd#1 +[Ctrl] Bkgd#2



Statistical Analysis

- **Tolerance Limits**
 - Field usefulness
- **Tukey's Multiple Comparisons**
 - Location Analysis
- **Spearman-Rank Correlation**
 - Age Analysis
- **Bivariate Normal Correlation**
 - Sample pump flow rate
- **Cluster Analysis**



- 764

50 ppb Results

Parts Per Billion

450
400
350
300
250
200
150
100
50
0

1,1-Dichloroethene
Chloroethane
cis-1,2-Dichloroethene
1,3-Butadiene
m&p-Xylene
Freon 11
Vinyl chloride
Tetrachloroethene
Carbon tetrachloride
Chloroform
Trichloroethene
3-Chloro-1-Propene
1,3-Dichlorobenzene
Methylene chloride
1,2-DCTFE
1,1,1-Trichloroethane
Benzene
Ethylbenzene
Toluene
o-Xylene
Chloromethane
Chlorobenzene
1,1-Dichloroethane
1,4-Dichlorobenzene
1,2-Dichloropropane
1,3,5-Trimethylbenzene
1,2-Dichloroethane
1,2,4-Trimethylbenzene
Freon 113
p-Ethyltoluene
Hexachlorobutadiene
Styrene
1,2-Dichlorobenzene
1,2,4-Trichlorobenzene
Methyl bromide

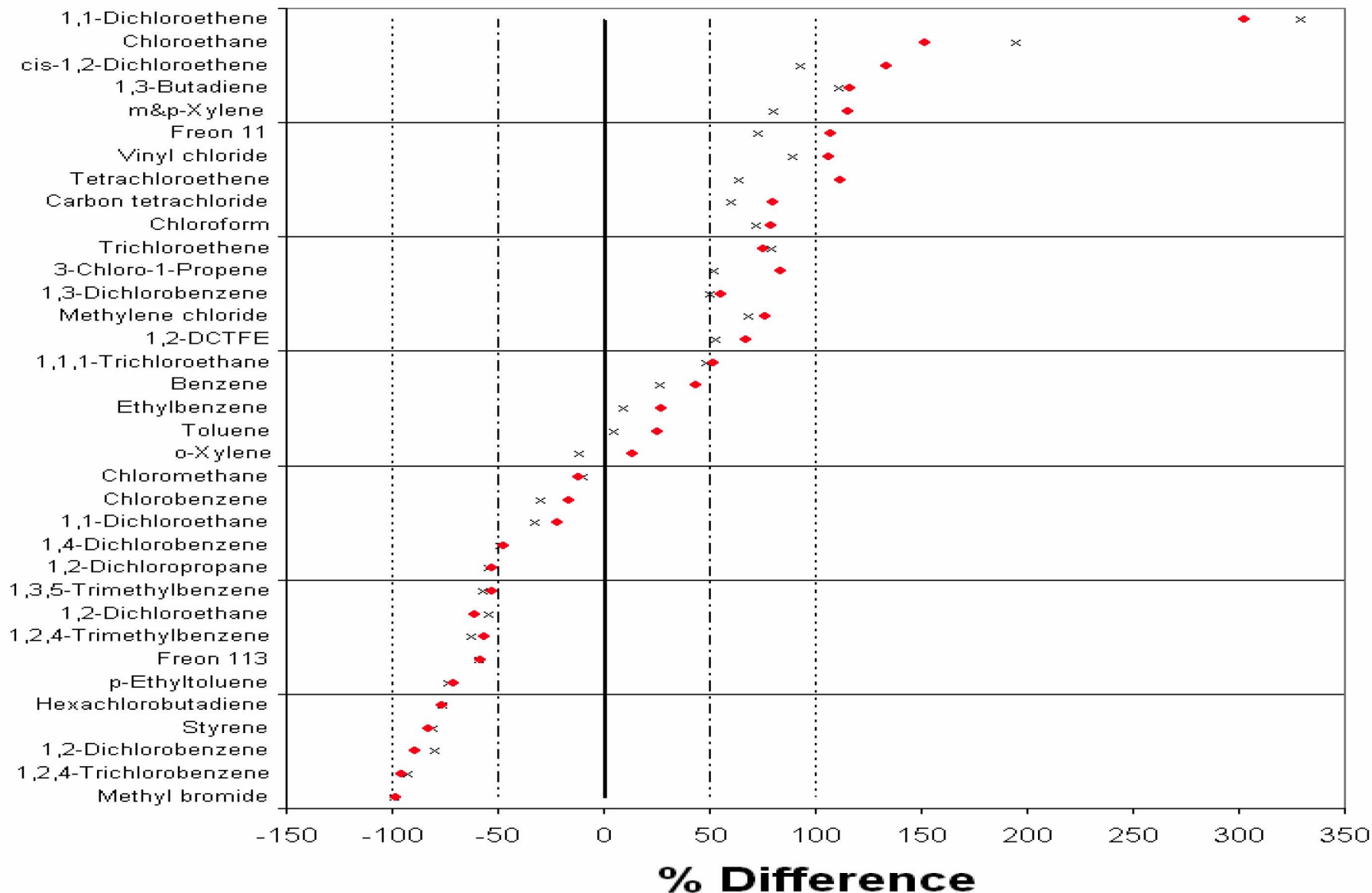


200 ppb Results



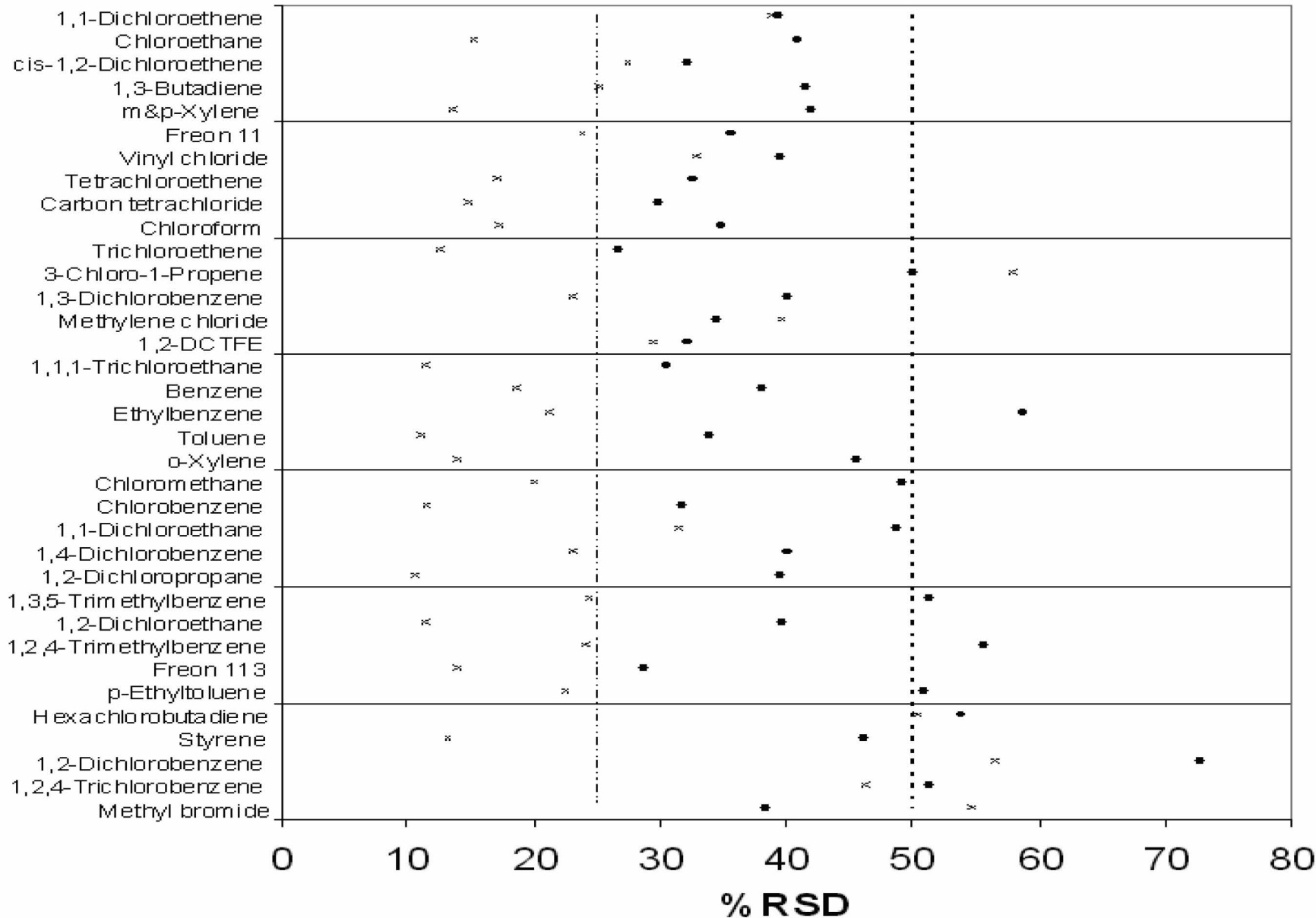


Accuracy





Precision



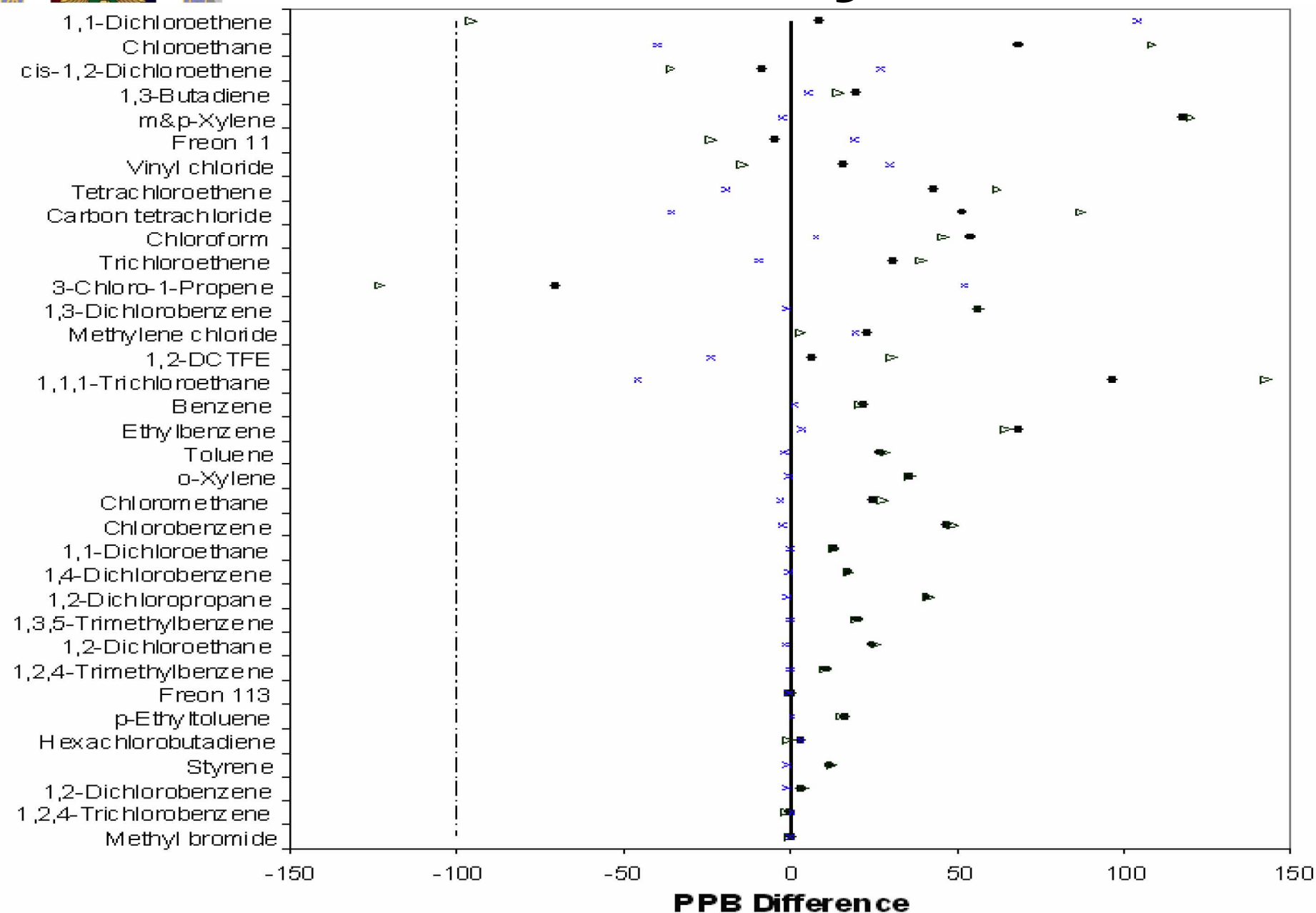


Location Analysis

- **Compared the Three Locations to determine possible trends**
 - Graphical Comparison at each concentration by chemical
 - Statistical Comparison at each concentration – Tukey's Multiple Comparisons



Location Analysis 50 PPB



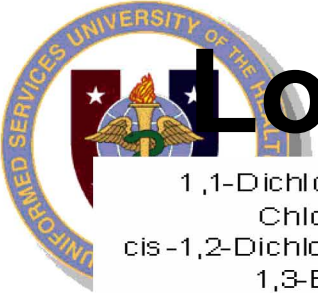


Location Analysis

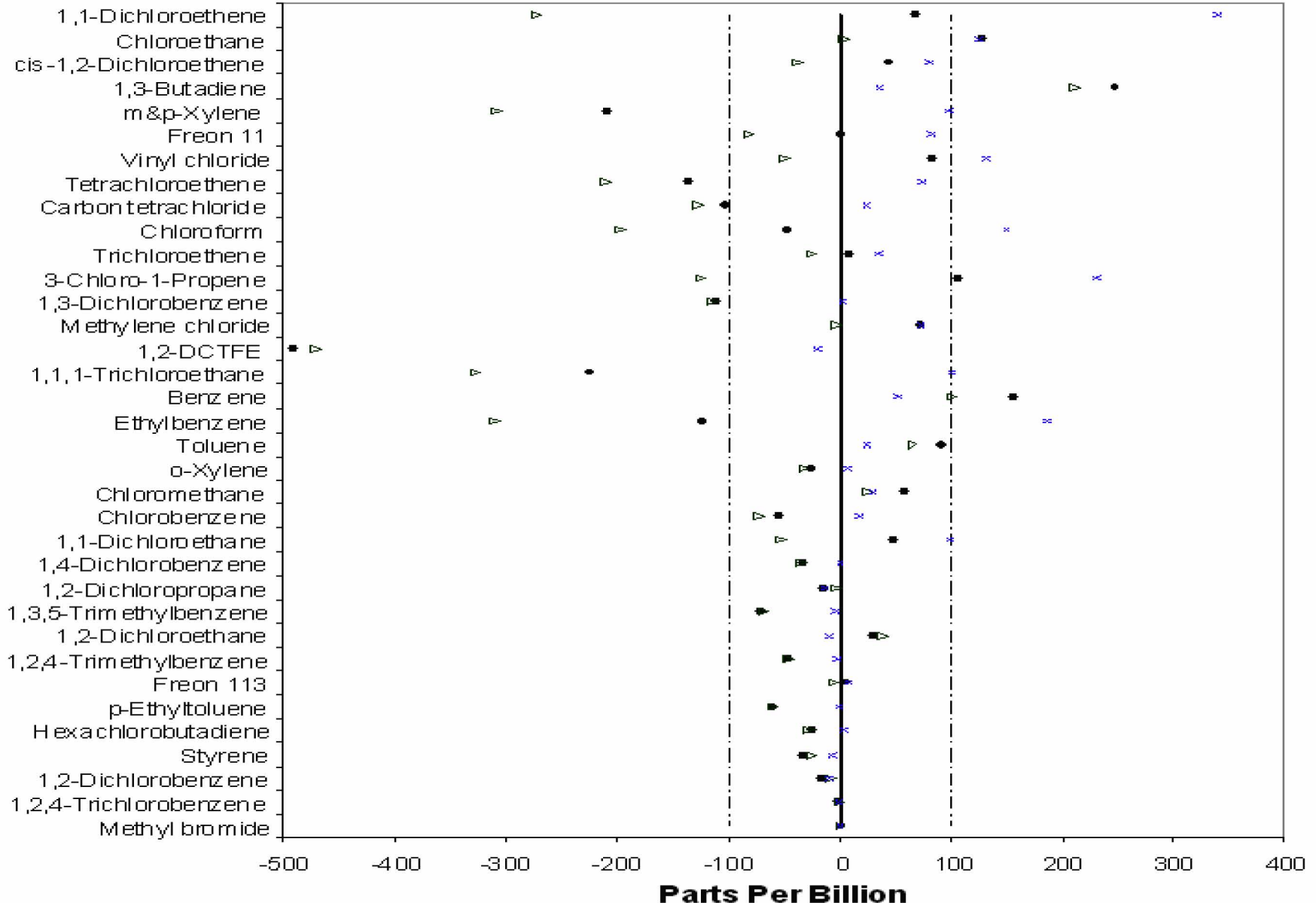
50 ppb

Mean Difference

(I) Location	(J) Location	(I-J)	Std. Error	Sig.
Ft. Leonard Wood	San Antonio	25.21	6.39	0.00
	Syracuse	22.86	6.39	0.00
San Antonio	Ft. Leonard Wood	-25.21	6.39	0.00
	Syracuse	-2.35	6.39	0.93
Syracuse	Ft. Leonard Wood	-22.86	6.39	0.00
	San Antonio	2.35	6.39	0.93



Location Analysis 200 PPB





Location Analysis

200 ppb

		Mean Difference		
(I) Location	(J) Location	(I-J)	Std. Error	Sig.
Ft. Leonard Wood	San Antonio	-20.62	19.67	0.55
	Syracuse	-76.05	19.67	0.00
San Antonio	Ft. Leonard Wood	20.62	19.67	0.55
	Syracuse	-55.43	19.67	0.02
Syracuse	Ft. Leonard Wood	76.05	19.67	0.00
	San Antonio	55.43	19.67	0.02

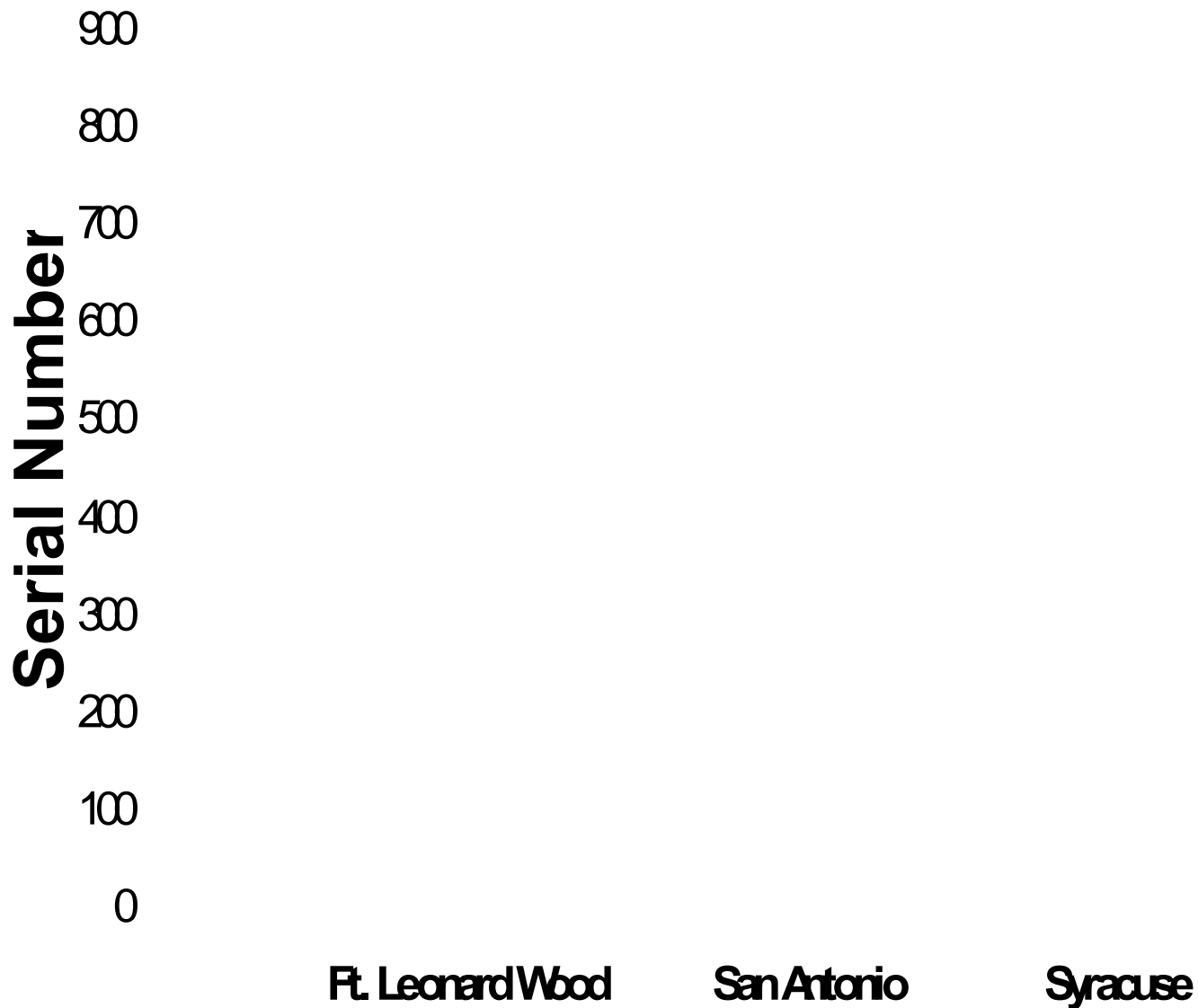


Age Analysis

- **Correlation between Age and Response**
 - Instrument Serial Number represented Age
 - Average concentration estimate for the 35 chemicals



Serial Numbers (Age) By Location





Two-tailed t-test, $\alpha=0.05$

Spearman Rank Correlations	correlation value	p-value
Age and 50ppb data	-0.2109	0.1548
Age and 200 ppb data	-0.2766	0.0518



Sample Pump Flow Rate Analysis



- **Flow measured with Bios DryCal**
- **Expected flow – 100 ml/min**
 - 10 instruments – 95-105 ml/min
 - Total Range – 49-123 ml/min
- **Variance Comparison**
 - 10 instruments – 16 - 17 %RSD
 - All instruments – 25 - 41 %RSD



Sample Pump Flow Rate Analysis

Two-tailed t-test, $\alpha=0.05$

Bivariate Normal Correlations	correlation value	p-value
Flow rate and 50 ppb	0.4217	0.0054
Flow rate and 200 ppb	0.2720	0.0814



Cluster Analysis

- **Determined response similarity between chemicals**
 - Multi-chlorinated benzene compounds
 - Not 1,3-dichlorobenzene
 - Trimethylbenzene compounds
 - No similarities in chlorinated alkanes



Study Limitations

- **Different Tuning Procedure Effects**
- **Accuracy Assessment**
 - Exact concentrations in the test mixture
 - Testing the laboratory set-up
- **Serial Numbers Representing Age**



Conclusions

- **Best-fit Calibration Curve**
 - Improved Accuracy
- **25 to 41 %RSD**
 - Multi-laboratory test = 25 %RSD
 - Usable quantitative result on-scene
- **Sample Pump Flow Rate Control Reduced Variability**



Conclusions

- **No definite findings on Age**
 - Serial number is limited as variable
 - Date of last maintenance – better variable
- **Location effects**
 - No consistent result for the two concentrations

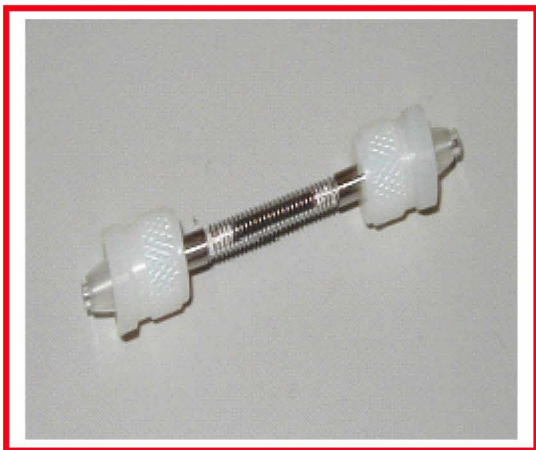


Recommendations

- **Control the sample pump flow rate on all instruments**
 - Re-create the calibration curves
- **Test age effects using last maintenance date**



Questions?



<http://www.portagas.com/diagram2.gif>

